

EC Harmonization Programme for Air Quality Measurements:

The evaluation of the Intercomparison Exercise for SO₂, CO, O₃, NO and NO₂ 13.- 16. October 2008

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WHO COLLABORATING CENTRE FOR AIR QUALITY
MANAGEMENT AND AIR POLLUTION CONTROL

at the

FEDERAL ENVIRONMENTAL AGENCY



Executive Summary

From the 13th to the 16th of October 2008 in Ispra (IT), 5 AQUILA (Network of European Air Quality Reference Laboratories) and 2 laboratories of the World Health Organisations (WHO) Euro-Region met at an intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO₂, CO, NO, NO₂ and O₃).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

In terms of criteria imposed by the European Commission, 44% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 56% of the results had good measured values, but the reported uncertainties were either too small (54%) or too high (2%).

The comparability of results among AQUILA participants is satisfactory for O₃, CO, NO₂ and NO measurement method, but the pollutant SO₂ needs further improvements and harmonization programmes.

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Abbreviations:

AQUILA	Network of National Reference Laboratories for Air Quality
CO	Carbon monoxide
DQO	Data Quality Objective
ERLAP	European Reference Laboratory of Air Pollution
EC	European Commission
GPT	Gas phase titration
IE	Intercomparison Exercise
IES	Institute for Environment and Sustainability
ISO	International Organization for Standardization
JRC	Joint Research Centre
NO	Nitrogen monoxide
NO ₂	Nitrogen dioxide
NO _x	the oxides of nitrogen, the sum of NO and NO ₂
NRL	National Reference Laboratory
O ₃	Ozone
SO ₂	Sulphur dioxide
WHO	World Health Organization Collaborating Centre for Air Quality
CC-EURO	Management and Air Pollution Control, Berlin

Mathematical Symbols:

<i>symbol</i>	<i>explanation</i>
α	converter efficiency (EN 14211; [9])
E_n	E_n – number statistic (ISO 13528; [18])
r	repeatability limit (ISO 5725; [19])
R	reproducibility limit (ISO 5725; [19])
σ_p	the standard deviation for proficiency assessment (ISO 13528; [18])
x^*	robust average (Annex C ISO 13528; [18])
s^*	robust standard deviation (Annex C ISO 13528; [18])
s_r	repeatability standard deviation (ISO 5725; [19])
s_R	reproducibility standard deviation (ISO 5725; [19])
U_X	The expended uncertainty of the assigned/reference value (ISO 13528; [18])
U_{xi}	The expended uncertainty of the participant's value
u_X	The standard uncertainty of the assigned/reference value (ISO 13528; [18])
X	Assigned/reference value (ISO 13528; [18])
x_i	the average of three values reported by the participant i (for particular parameter and concentration level) (ISO 5725; [19])
$x_{i,j}$	j -th reported value of participant i (for particular parameter and concentration level) (ISO 5725; [19])
z'	z' -score statistic (ISO 13528; [18])

1. Introduction

As the old “Framework Directive” [1] and its “Daughter Directives” [2], [3], [4] and [5], the new Directive 2008/50/EC [6] on ambient air quality and cleaner air for Europe sets a framework for a harmonized air quality assessment in Europe. One important objective of the Directive is that the ambient air quality shall be assessed on the basis of common methods and criteria. It deals with the air pollutants sulphur dioxide (SO₂), nitrogen dioxide (NO₂) and monoxide (NO), particulate matter, lead, benzene, carbon monoxide (CO) and ozone (O₃). Among others it specifies the reference methods for measurements and Data Quality Objectives (DQO) for the accuracy of measurements.

The European Commission (EC) has supported the development and publication of reference measurement methods [7], [8], [9] and [10] as European standards. Appropriate calibration methods [11], [12] and [13] have been standardised by the International Organization for Standardization (ISO).

As foreseen in the new Directive, the European Reference Laboratory of Air Pollution (ERLAP) of the Institute for Environment and Sustainability (IES) at the Joint Research Centre (JRC) organizes intercomparison exercises (IE) to assess and improve the status of comparability of measurements of National Reference Laboratories (NRL) of each Member State of the European Union.

The World Health Organization Collaborating Centre for Air Quality Management and Air Pollution Control, Berlin (WHO CC) is carrying out similar activities since 1994 [14] [15], but with a view to obtaining harmonized air quality data for health related studies. Their program integrates within the WHO EURO region, which includes public health institutes and other national institutes - especially from the Central Eastern Europe, Caucasus and countries from Central Asia.

Starting in 2004, it has been decided to bring together the efforts of both the JRC-ERLAP and WHO CC and to coordinate activities as far as possible, with a view to optimize resources and have better international harmonization. The following report deals with the IE that took place from the 13th to the 16th of October 2008 in Ispra (IT) in joint cooperation of EC/ JRC/IES/ERLAP and WHO CC.

ERLAP has been organizing IEs since 1990 aiming at evaluating the comparability of measurements carried out by NRLs and promoting information exchange among the expert laboratories. Nowadays the main objective, in accordance with the Network of National Reference Laboratories for Air Quality (AQUILA) [16], comprises a more systematic approach that offers alert mechanism for the purposes of the EC and is also useful to NRLs in quality assurance of their implemented quality systems. The methodology of organization of IEs was developed by ERLAP and is described in a position paper on the organization of intercomparison exercises for gaseous air pollutants [17]. This position paper is currently a proposal to the AQUILA and the final agreement of position paper is foreseen to take place during 2008. Then it will be applied throughout all future IEs.

The evaluation scheme applied to this IE is described in detail in the position paper [17] and it reflects the inputs given by AQUILA. Firstly, it was acknowledged that the evaluation scheme should have common criteria, to alert the EC on the possible performance failure, and not to base these alerts on claimed uncertainty of participants. For that purpose the common criterion was proposed to AQUILA and the z'-score method [18] was implemented in to the evaluation scheme. The common criterion is derived from the uncertainty requirements for calibration gases stated in the European standards [7], [8], [9] and [10], which are consistent with the DQOs of European Directives. In view of AQUILA, NRLs with overall unsatisfactory results of the z'-score evaluation (one unsatisfactory or two questionable results per parameter) are required to repeat their participation to the next IE in order to demonstrate remediation measures [17]. Secondly, it was acknowledged that the evaluation scheme

should be useful to participants accredited according to ISO 17025 and thus should include measurement uncertainty of participants. For that purpose, participants measurement results (measurement values and uncertainties) are compared to assigned values applying the E_n – number method [18].

Beside the proficiency of participating laboratories the repeatability and reproducibility of standardized measurement methods [19], [20] and [21] are evaluated as well. These group evaluations will be used in a separate communication as the indicators of trends of quality of measurements over different IEs undertaken by ERLAP.

2. Communication and time schedule

The IE was announced in November 2007 to the members of the AQUILA network and the WHO CC representative. A registration letter was sent to interested parties and the registration was closed in June 2008 with the list of 8 participating laboratories. The participants were required to bring their own measurement instruments, data acquisition equipment and travelling standards (to be used for calibrations or checks during the IE).

The participants were invited to arrive on Monday, 13th October 2008, for the installation of their equipment. The calibration of NO_x and O₃ analysers was carried out on Tuesday morning and the generation of NO_x and O₃ gas mixtures started at 11:00. The calibration of SO₂ and CO analysers was carried out on Wednesday 18:00 and the generation of CO and SO₂ gas mixtures started at 20:00. The test gases generation finished on Thursday at 7:00 a.m..

3. Participants

All participants were organizations dealing with the routine ambient air monitoring or health related studies. The national representatives came from EU member states, Norway, Portugal, Slovak Republic and Sweden, and from Albania, Croatia and Turkey. One regional representative came from 'Port of Rotterdam area' (The Netherlands).

Table 1: The list of participating organizations.

Country	Name of Organization	IE code
Norway	Norwegian Institute for Air Research	A
Portugal	Agência Portuguesa do Ambiente	B
Slovak Republic	Slovak Hydrometeorological Institute	C
Sweden	Stockholm University	D
European Commission	European Reference Laboratory of Air Pollution	E
Albania	Institute of Energy, Water and Environment of Polytechnic University of Tirana	F
Croatia	Institute of Medical Research	G
The Netherlands	DCMR Environmental Protection Agency	H
Turkey	The Ministry of environment and forestry	

The representatives from Turkey attended the IE in the quality of observers.

4. The preparation of test mixtures

The ERLAP IE facility has been described in several reports [22] and [23]. During this IE, gas mixtures were prepared for SO₂, CO, O₃, NO and NO₂ at concentration levels around European Air Quality limit values, critical levels and assessment thresholds.

The test mixtures were prepared by the dilution of gases from cylinders containing high concentration of NO, SO₂ or CO using thermal mass flow controllers [13]. O₃ was added using an ozone generator and NO₂ was produced applying the gas phase titration method [24] in the conditions of excess NO.

The participants were required to report three half-hour-mean measurements for each concentration level in order to evaluate the repeatabilities of standardized measurement methods. Zero concentration levels were generated for one hour and one half-hour-mean measurement was reported. The sequence program of generated test gases is given in Table 2.

Table 2: The sequence program of generated test gases.

day	start time	duration	operation or number	run	zero air	NO	NO ₂	O ₃	CO	SO ₂
		(h)			(nmol/mol)	(nmol/mol)	(nmol/mol)	(nmol/mol)	(μmol/mol)	(nmol/mol)
13-Oct	12:00	6	installation							
14-Oct	08:00	3	calibration							
14-Oct	11:00	1	NO & NO ₂ & O ₃ run 0		0					
14-Oct	12:00	2	NO & NO ₂ run 1			500	0			
14-Oct	14:00	2	NO & NO ₂ run 2			380	120			
14-Oct	16:00	2	O ₃ run 1					120		
14-Oct	18:00	2	NO & NO ₂ run 3			250	0			
14-Oct	20:00	2	NO & NO ₂ run 4			146	104			
14-Oct	22:00	2	O ₃ run 2					104		
15-Oct	00:00	2	NO & NO ₂ run 5			150	0			
15-Oct	02:00	2	NO & NO ₂ run 6			90	60			
15-Oct	04:00	2	O ₃ run 3					60		
15-Oct	06:00	2	NO & NO ₂ run 7			50	0			
15-Oct	08:00	2	NO & NO ₂ run 8			29.1	20.9			
15-Oct	10:00	2	O ₃ run 4					20.9		
15-Oct	12:00	2	NO & NO ₂ run 9			15.7	0			
15-Oct	14:00	2	NO & NO ₂ run 10			2.1	13.6			
15-Oct	16:00	2	O ₃ run 5					13.6		
15-Oct	< 18:00	2	calibration							
15-Oct	20:00	1	CO & SO ₂ run 0		0					
15-Oct	21:00	2:30	CO & SO ₂ run 1						8.6	132
15-Oct	23:30	2	CO & SO ₂ run 2						6	47
16-Oct	01:30	2	CO & SO ₂ run 3						4.3	18.8
16-Oct	03:30	2	CO & SO ₂ run 4						2	7.5
16-Oct	05:30	2	CO & SO ₂ run 5						1	3
16-Oct	07:30	1			0					
16-Oct	08:30		END							

5. The evaluation of laboratory's measurement proficiency

To evaluate the participants measurement proficiency the methodology described in ISO 13528 [18] was applied. It has been agreed among the AQUILA members to take the measurement results of ERLAP as the assigned/reference values for the whole IE [17]. The traceability of ERLAP's measurement results and the method applied to validate them are presented in Annex A. In the following proficiency evaluations, the uncertainty of test gas homogeneity (Annex A) was added to the uncertainties of ERLAP's measurement results.

All data reported by participating laboratories are presented in Annex B.

As it is described in the position paper [17], the proficiency of the participants was assessed by calculating two performance indicators. The first performance indicator (z'-score) tests if the difference between the participants measured value and the assigned/reference value remains within the limits of a common criterion, while the second performance indicator (E_n-number) tests if the difference between the participants measured values and assigned/reference value remains within the limits of a criterion, that is calculated individually for each participant, from the uncertainty of the participants measurement result and the uncertainty of the assigned/reference value.

z' - score

The z' - score statistic is calculated according to ISO 13528 [18] as:

$$z' = \frac{x_i - X}{\sqrt{\sigma_p^2 + u_x^2}} = \frac{x_i - X}{\sqrt{(a \cdot X + b)^2 + u_x^2}} \quad (1)$$

where 'x_i' is a participant's run average value, 'X' is the assigned/reference value, 'σ_p' is the 'standard deviation for proficiency assessment' and 'u_x' is the standard uncertainty of assigned value. For 'a' and 'b' see Table 3.

In the European standards [6], [8], [9] and [10] the uncertainties for calibration gases used in ongoing quality control are prescribed. In fact, it is stated that the maximum permitted expanded uncertainty for calibration gases is 5% and that 'zero gas' shall not give instrument reading higher than the detection limit. As one of the tasks of NRLs is to supply calibration gas mixtures, the 'standard deviation for proficiency assessment' (σ_p) [18] is calculated in fitness-for-purpose manner from requirements given in European standards.

Over the whole measurement range σ_p is calculated by linear interpolation between 2.5% at the calibration point (75% of calibration range) and the limit of detection at zero concentration level. The limits of detection of studied measurement methods were evaluated from the data of previous IEs. The linear function parameters of σ_p are given in Table 3:

Table 3: The standard deviation for proficiency assessment as a linear function of concentration (c) with linear function parameters: slope (a) and intercept (b).

	σ _p =a·c+b	
	a	b
		nmol/mol
SO ₂	0.024	0.4
CO	0.023	100
O ₃	0.022	0.5
NO	0.025	0.35
NO ₂	0.023	0.46

During the November 2008 AQUILA meeting, σ_p was enlarged, to 1 ppb at zero concentration of SO₂, O₃, NO, NO₂, and approved. It has been agreed that this change is noted in all relevant and not yet published IE reports and applied to all future IEs.

The z'-score evaluation allows the following criteria to be used for the assessment of results:

- $|z'| \leq 2$ are designated satisfactory.
- $2 < |z'| \leq 3$ are designated questionable.
- $|z'| > 3$ are designated unsatisfactory. Scores falling in this range are very unusual and are taken to indicate that the cause of the event should be investigated and remedied.

The results of z'-score evaluation are presented in bar plots (Figure 1 to Figure 5) in which the z'-scores of each participant are grouped together, and assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines.

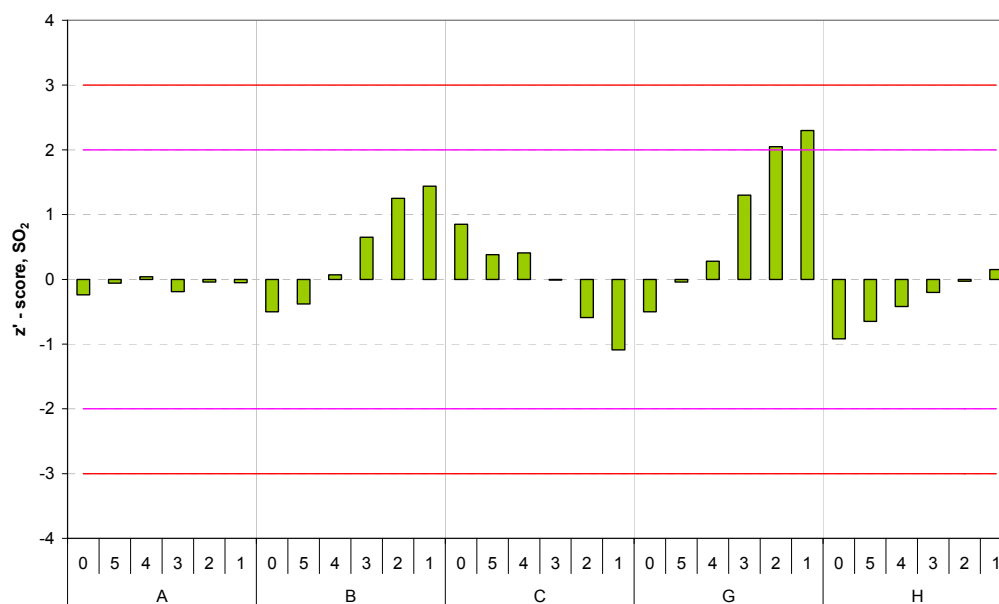


Figure 1: The z'-score evaluations of SO₂ measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (3 nmol/mol), 4 (7 nmol/mol), 3 (19 nmol/mol), 2 (47 nmol/mol), 1 (132 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

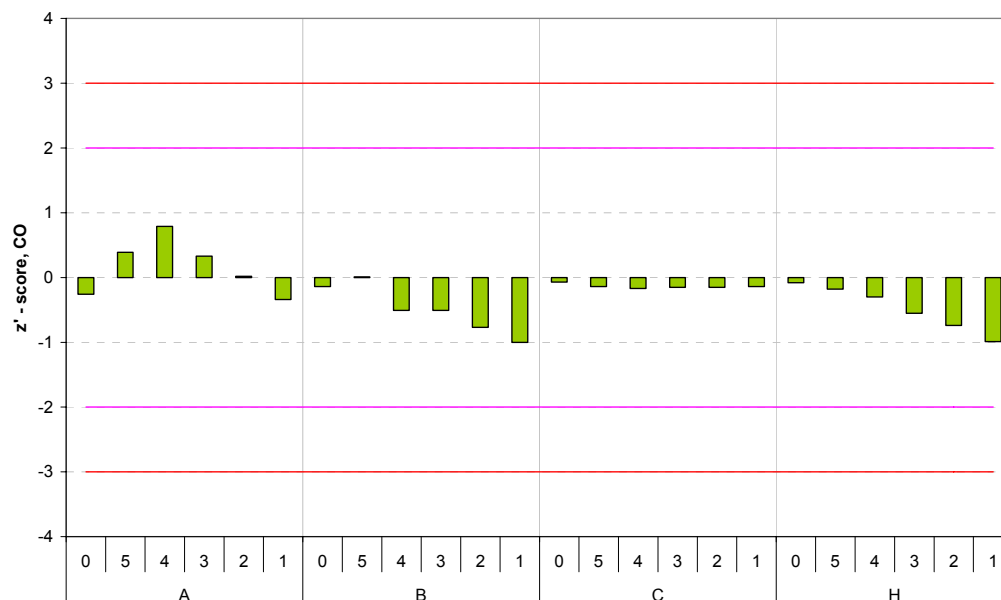


Figure 2: The z'-score evaluations of CO measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 µmol/mol), 5 (1 µmol/mol), 4 (2 µmol/mol), 3 (4 µmol/mol), 2 (6 µmol/mol), 1 (9 µmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

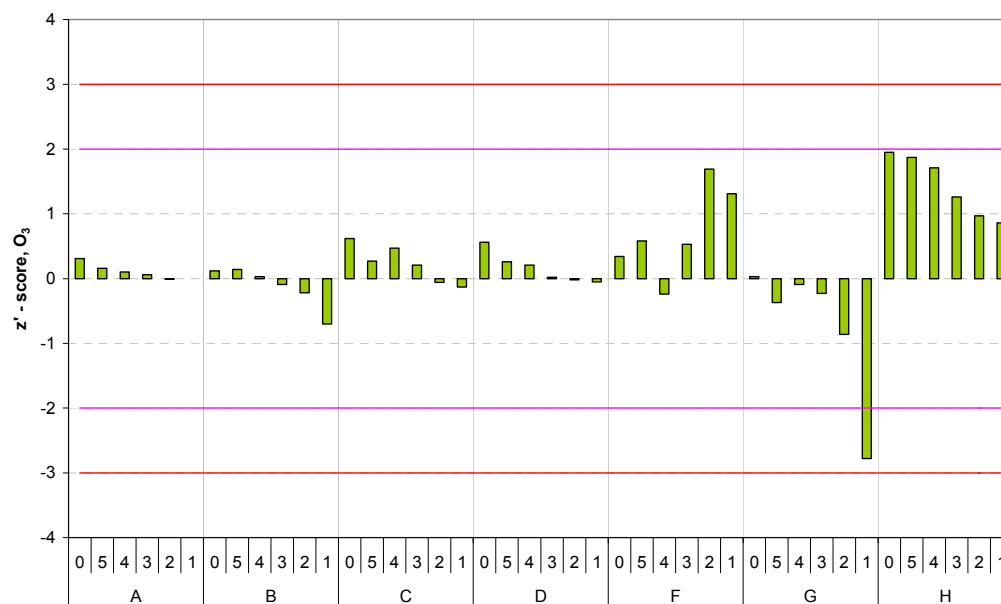


Figure 3: The z'-score evaluations of O₃ measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 5 (14 nmol/mol), 4 (21 nmol/mol), 3 (60 nmol/mol), 2 (104 nmol/mol), 1 (120 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

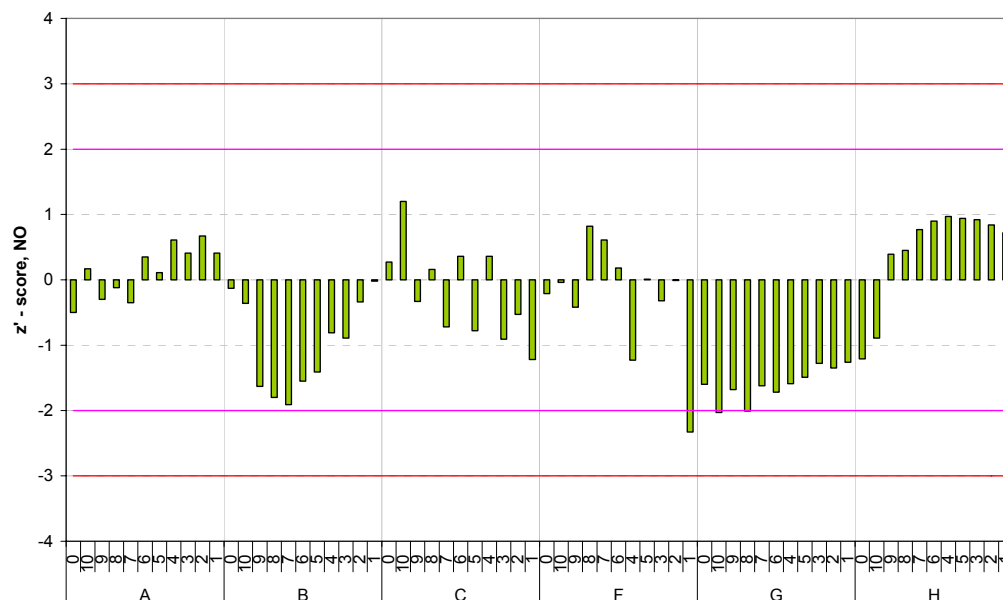


Figure 4: The z'-score evaluations of NO measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (2 nmol/mol), 9 (16 nmol/mol), 8 (30 nmol/mol), 7 (50 nmol/mol) , 6 (90 nmol/mol) , 5 (150 nmol/mol) , 4 (150 nmol/mol) , 3 (250 nmol/mol) , 2 (380 nmol/mol), 1 (500 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

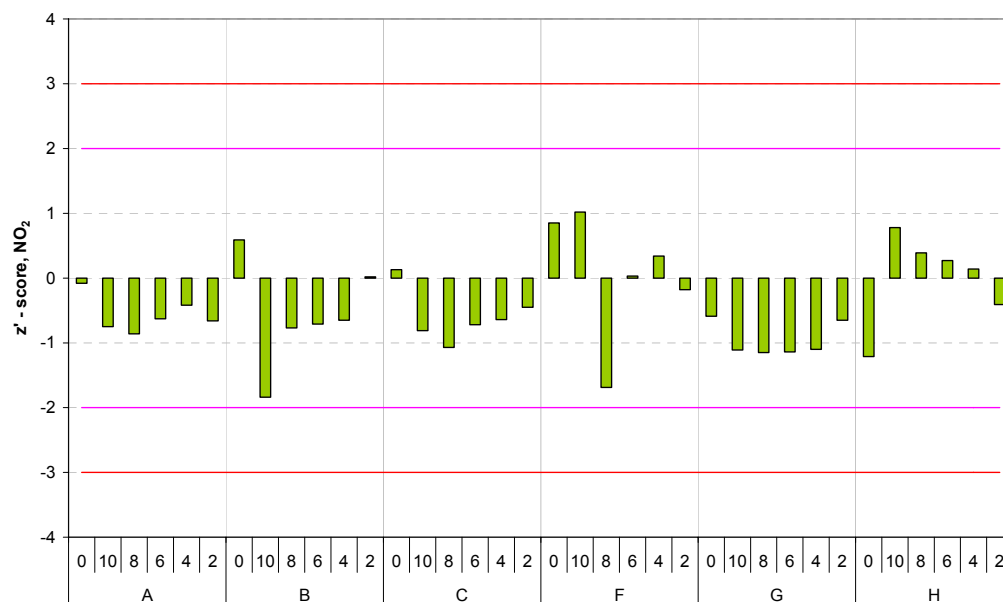


Figure 5: The z'-score evaluations of NO₂ measurements
are given for each participant and each tested concentration level. The evaluations are in the order of increasing concentrations (run number order (with nominal concentration) is: 0 (0 nmol/mol), 10 (14 nmol/mol), 8 (21 nmol/mol), 6 (60 nmol/mol), 4 (104 nmol/mol), 2 (120 nmol/mol)). The assessment criteria are presented as $z'=\pm 2$ and $z'=\pm 3$ lines. They represent the limits for the questionable and unsatisfactory results.

E_n - number

The normalised deviations [18] (E_n) were calculated according to:

$$E_n = \frac{x_i - X}{\sqrt{U_{x_i}^2 + U_X^2}} \quad (2)$$

where 'X' is the assigned/reference value with an expanded uncertainty 'U_X' and 'x_i' is the participant's average value with an expanded uncertainty 'U_{x_i}'. Satisfactory results are the ones for which $|E_n| \leq 1$.

In Figure 6 to Figure 10 the biases of each participant (x_i-X) are plotted and error bars are used to denote the value of denominator of equation 2 ($\sqrt{U_{x_i}^2 + U_X^2}$). These plots represent also the E_n-number evaluations where, considering the E_n criteria ($|E_n| \leq 1$), all results with error bars touching or crossing x-axis are satisfactory. Reported standard uncertainties (Annex B) that are bigger than "standard deviation for proficiency assessments" (σ_p, Table 3) are considered not fit-for-purpose and are denoted with "*" in the x-axis of each figure.

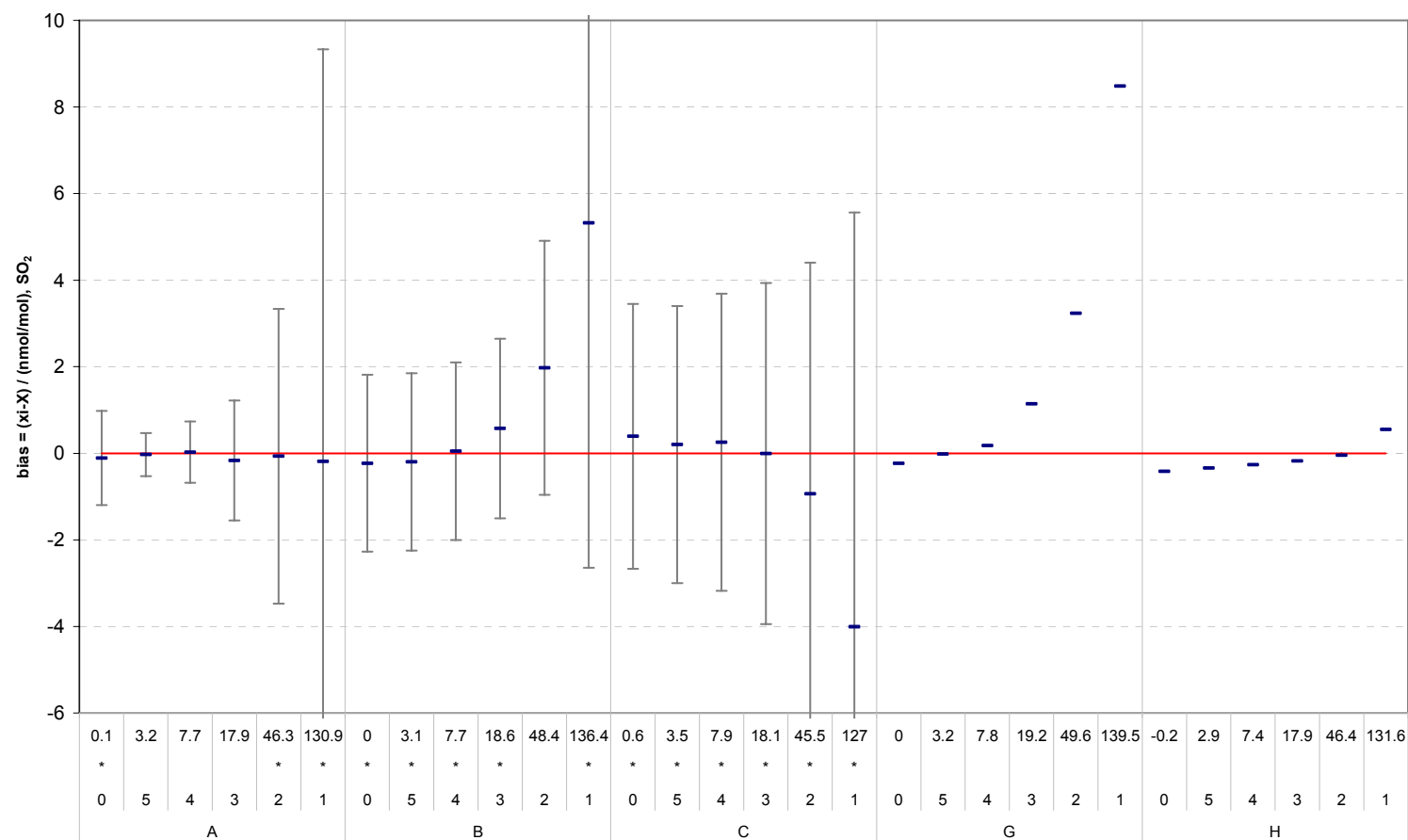


Figure 6: Bias of participant's SO₂ measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. The results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The "*" mark indicates reported standard uncertainties bigger then σ_p .

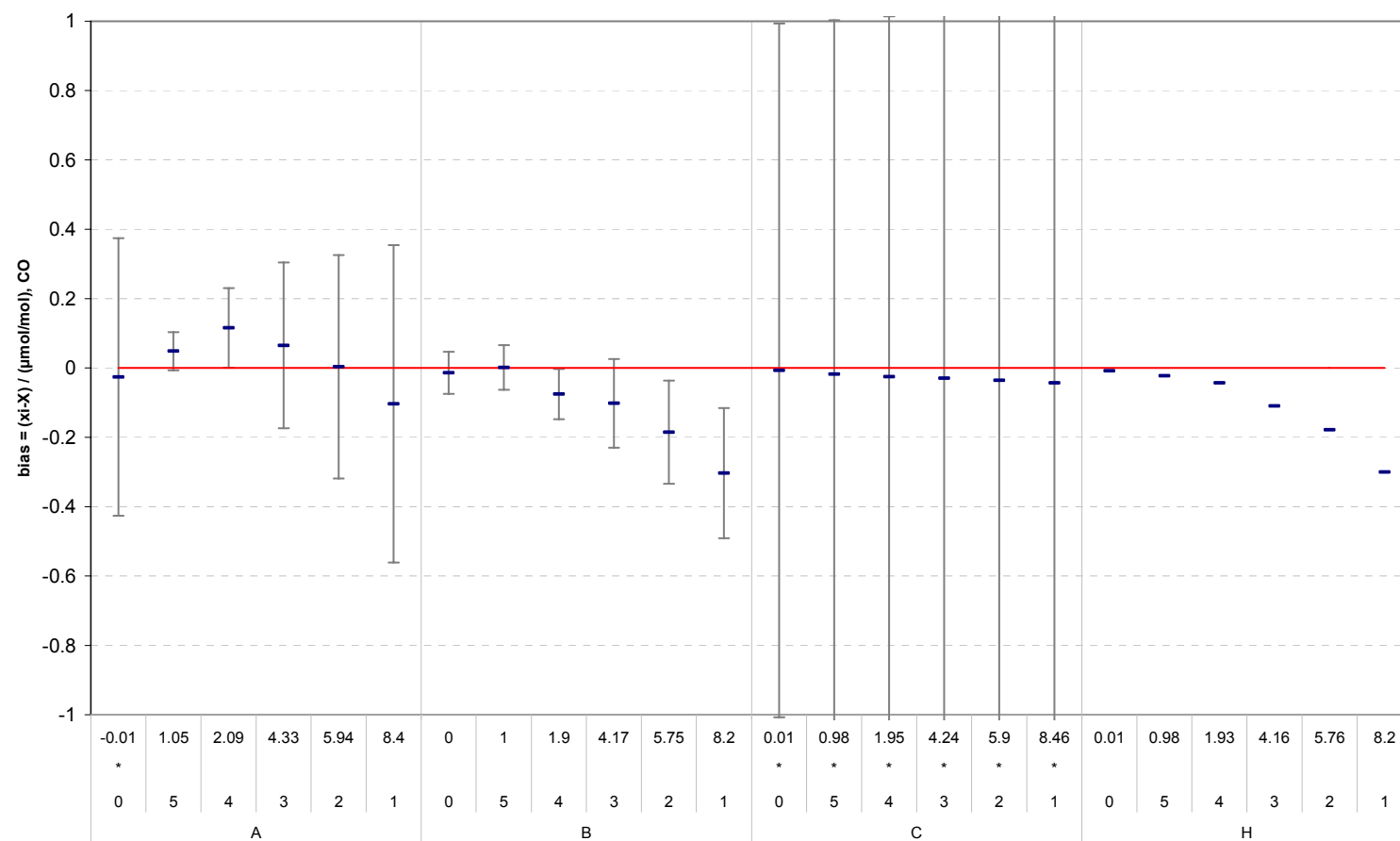


Figure 7: Bias of participant's CO measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (μmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p .

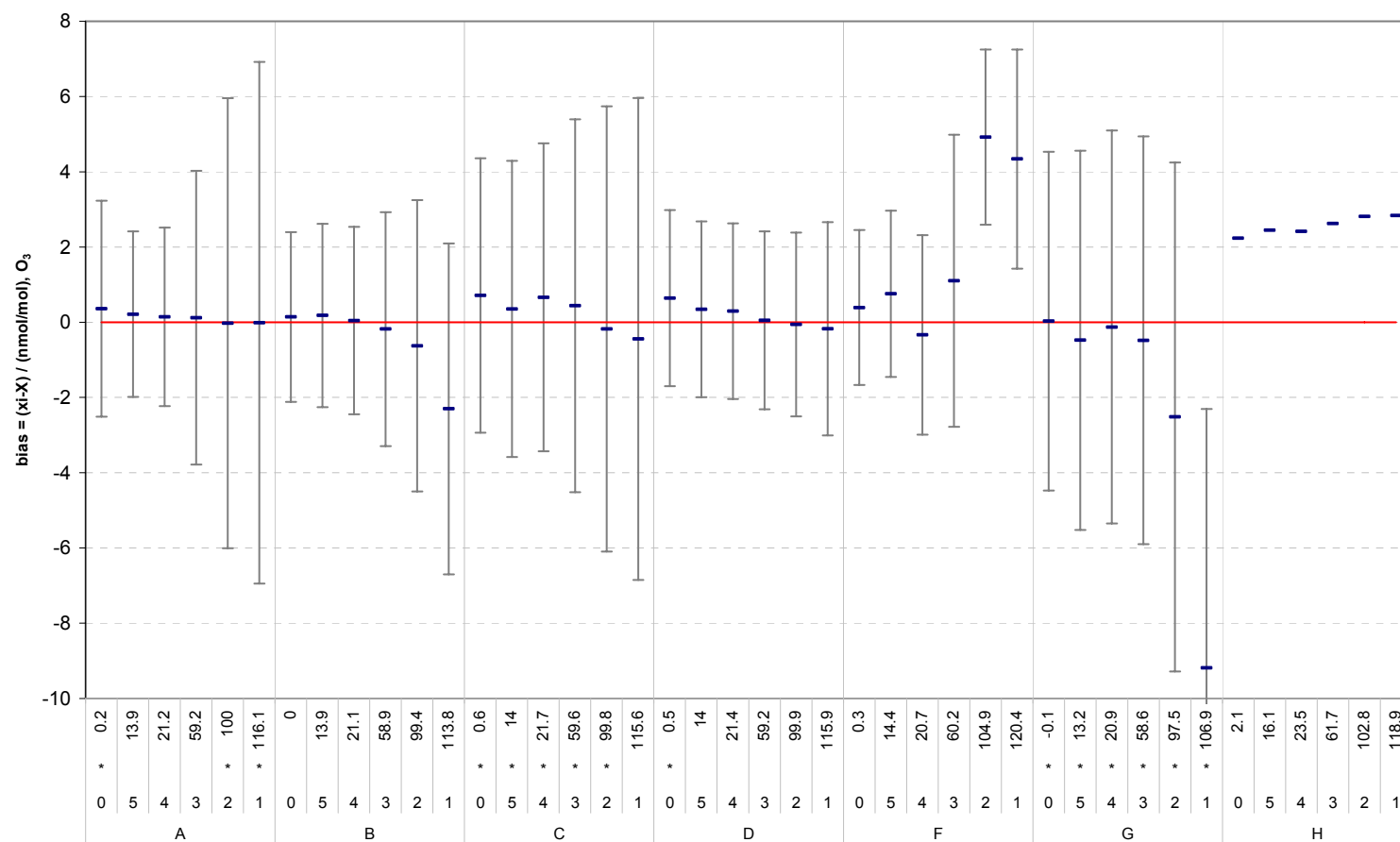


Figure 8: Bias of participant's O₃ measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger then σ_p .

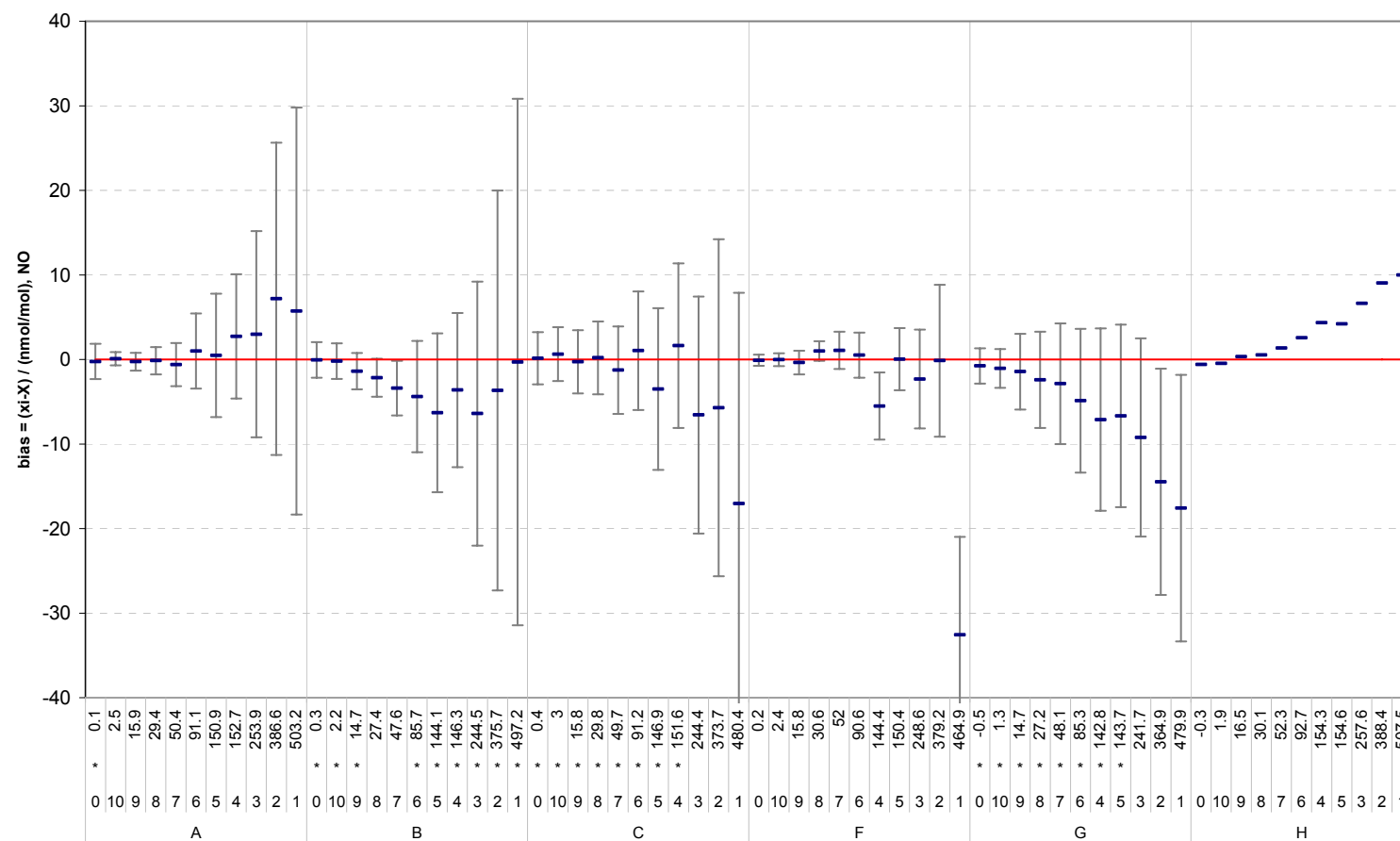


Figure 9: Bias of participant's NO measurement results
together with the expanded uncertainty of bias presented with error bar are given for each tested concentration level. Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number (numbers 0 to 5) together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p .

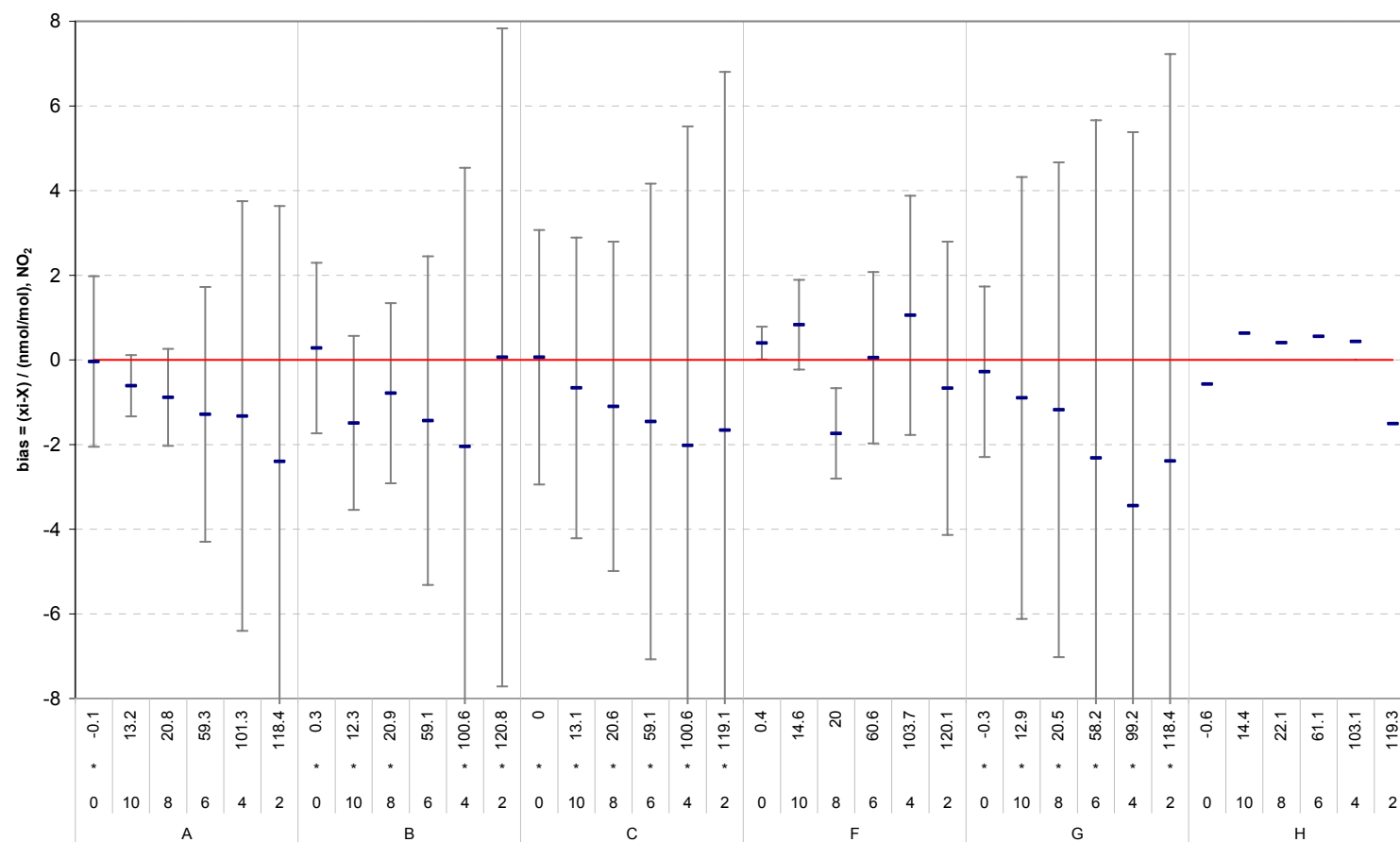


Figure 10: Bias of participant's NO₂ measurement results
together with the expanded uncertainty of bias presented with error bar are given for tested concentration levels with NO₂ run numbers 0, 2, 4, 6, 8 and 10 (see Table 2). Results with error bars touching or crossing the x-axis are satisfactory. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given. The '*' mark indicates reported standard uncertainties bigger than σ_p .

6. Performance characteristics of individual laboratories

Individual participants' biases were evaluated and are presented in chapter 5 (Figure 6-Figure 10). Since the results of NO₂ runs 1,3,5,7 and 9 were not treated in proficiency evaluation the biases of these runs are presented in Figure 11.

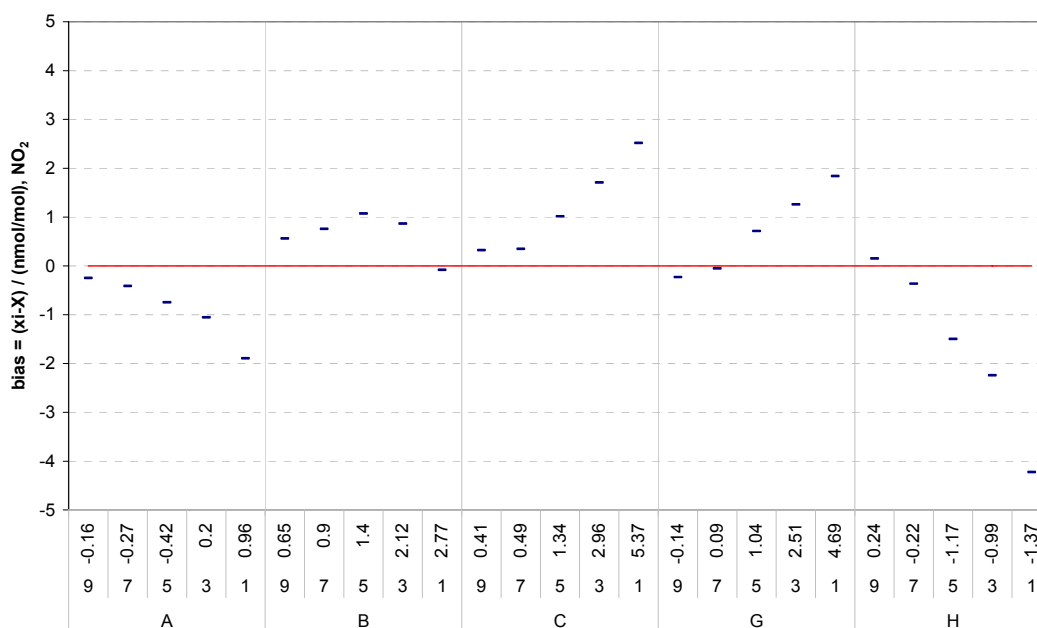


Figure 11: Bias of participant's NO₂ measurements for run numbers 1, 3, 5, 7 and 9

At these test gas mixtures the concentration levels of NO₂ were zero and the concentration levels of NO were not zero (see Table 2). In that perspective the figure shows the effect of NO concentration on NO₂ measurements. For each evaluation the run number together with the participants rounded run average (nmol/mol) is given.

The efficiency of NO₂-to-NO converters of NO_x analyzers

Since NO and NO₂ test gases were produced by gas phase titration it is possible to evaluate the efficiency of NO₂-to-NO converter of each participant's NO_x analyser. The evaluation takes each participants NO and NO₂ measurements before and after oxidation by O₃. The converter efficiency (α) is calculated using equation 3 [9]:

$$\alpha = \frac{[NO_2]_i - [NO_2]_{i-1}}{[NO]_{i-1} - [NO]_i} \cdot 100\% \quad (3)$$

The O₃ measurements of each participant can also be compared to either NO or NO₂ change by calculating Δ^{NO} or Δ^{NO_2} using equation 4 and 5 respectively:

$$\Delta^{NO} = [O_3]_{i+1} - ([NO]_{i-1} - [NO]_i) \quad (4)$$

$$\Delta^{NO_2} = [O_3]_{i+1} - ([NO_2]_i - [NO_2]_{i-1}) \quad (5)$$

Ideal value for α is 100% while for Δ^{NO} and Δ^{NO_2} it is 0 nmol/mol.

The evaluations of equation 4 and 5 can not be made for the forth GPT test (at 14 ppb of NO₂), because O₃ was not completely reduced due to insufficient excess of NO. The evaluations of equations 3, 4 and 5 for each participant at different concentration levels are given in Table 4.

Table 4: The efficiency of NO₂-to-NO converters.

IE	NO ₂	α	Δ^{NO}	Δ^{NO_2}
code	nmol/mol	%	nmol/mol	nmol/mol
A	14	99.5		
A	22	100.7	0.3	0.1
A	60	99.9	-0.5	-0.4
A	100	99.9	-1.3	-1.2
A	120	100.6	-0.6	-1.3
B	14	92.8		
B	22	99.2	0.9	1.1
B	60	98.9	0.6	1.2
B	100	100.3	1.2	0.9
B	120	97.2	-7.7	-4.3
C	14	99.1		
C	22	100.9	1.8	1.6
C	60	103.6	3.8	1.8
C	100	105.3	7.0	2.1
C	120	106.5	8.9	1.9
E	14	99.6		
E	22	100.8	-0.3	-0.5
E	60	99.9	-1.1	-1.1
E	100	100.4	-1.0	-1.4
E	120	99.8	-2.0	-1.8
G	14	97.3		
G	22	97.5	0.0	0.5
G	60	97.8	0.2	1.5
G	100	97.8	-1.4	0.8
G	120	98.9	-8.1	-6.8
H	14	97.4		
H	22	100.5	1.3	1.2
H	60	100.6	-0.2	-0.5
H	100	100.8	-0.5	-1.3
H	120	101.3	-0.2	-1.7

The uncertainty of converter efficiency evaluation at higher NO₂ concentration is smaller than at lower NO₂ concentration. For the general feeling, the average standard uncertainty of the converter efficiency is calculated, by taking standard deviations of repeatable measurements of quantities in equation 3, and is evaluated to approximately 1%, at 120 nmol/mol of NO₂, and 2%, at 14 nmol/mol of NO₂.

7. Discussion

For a general assessment of the quality of each result a decision diagram was developed (Figure 12) that categorises results in seven categories (a1 to a7). The general comments for each category are:

- a1: measurement result is completely satisfactory
- a2: measurement result is satisfactory (z'-score satisfactory and En-number ok) but the reported uncertainty is too high
- a3: measured value is satisfactory (z'-score satisfactory) but the reported uncertainty is underestimated (En-number not ok)
- a4: measurement result is questionable (z'-score questionable) but due to a high reported uncertainty can be considered valid (En-number ok)
- a5: measurement result is questionable (z'-score questionable and En-number not ok)
- a6: measurement result is unsatisfactory (z'-score unsatisfactory) but due to a high reported uncertainty can be considered valid (En-number ok)
- a7: measurement result is unsatisfactory (z'-score unsatisfactory and En-number not ok)

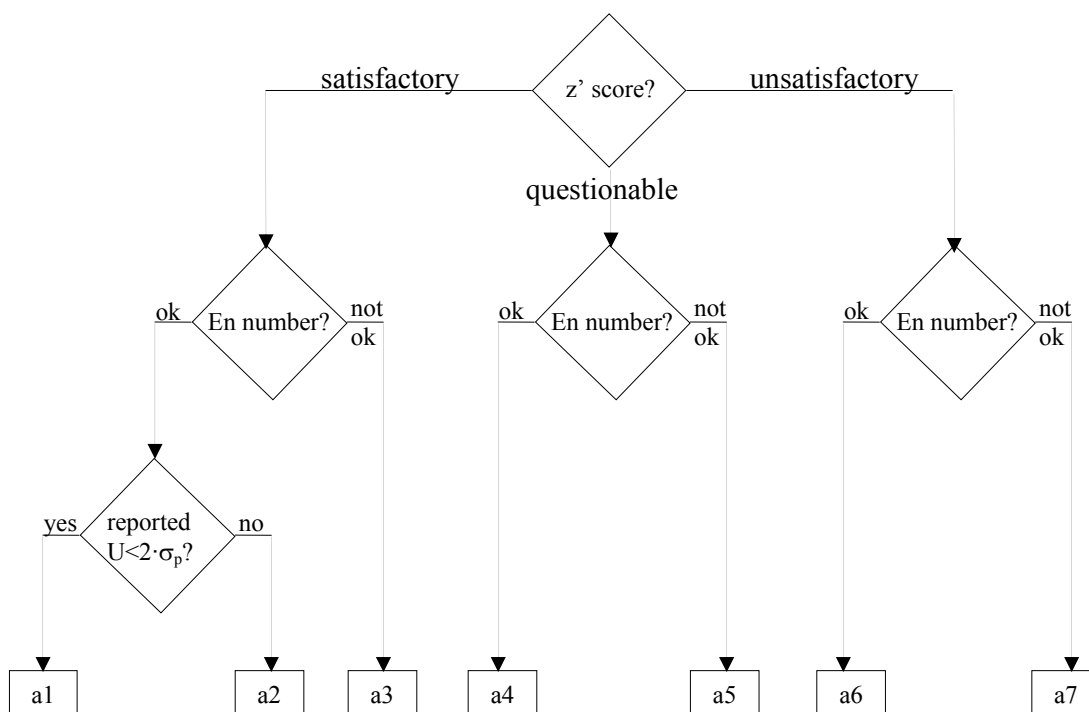


Figure 12: The decision diagram for general assessment of proficiency results.

The results of the IE were assigned to categories according to the diagram given in Figure 12 and are presented in Table 5. For clarity reasons, notation 'a1' is not inserted in Table 5 and all empty spaces represent 'a1' results.

Table 5: The general assessment of proficiency results.

Empty spaces represent 'a1' results while results not reported are represented by 'nv' (no value).

	run number	conc. level	IE code							
			A	B	C	D	F	G	H	
SO ₂ (nmol/mol)	0	0.2	a2	a2	a2	nv	nv	a3	a3	
	5	3.3		a2	a2	nv	nv	a3	a3	
	4	7.7		a2	a2	nv	nv	a3	a3	
	3	18.1		a2	a2	nv	nv	a3	a3	
	2	46.4	a2		a2	nv	nv	a5	a3	
	1	131.1	a2	a2	a2	nv	nv	a5	a3	
CO (μmol/mol)	0	0.014	a2		a2	nv	nv	nv	a3	
	5	0.999			a2	nv	nv	nv	a3	
	4	1.975			a2	nv	nv	nv	a3	
	3	4.269			a2	nv	nv	nv	a3	
	2	5.935		a3	a2	nv	nv	nv	a3	
	1	8.503		a3	a2	nv	nv	nv	a3	
O ₃ (nmol/mol)	0	-0.1	a2		a2	a2		a2	a3	
	5	13.7			a2			a2	a3	
	4	21.1			a2			a2	a3	
	3	59.1			a2			a2	a3	
	2	100.0	a2		a2		a3	a2	a3	
	1	116.1	a2				a3	a5	a3	
NO (nmol/mol)	0	0.3	a2	a2	a2	nv		a2	a3	
	10	2.4		a2	a2	nv		a4	a3	
	9	16.1		a2	a2	nv		a2	a3	
	8	29.6			a2	nv		a4	a3	
	7	51.0			a2	nv		a2	a3	
	6	90.1		a2	a2	nv		a2	a3	
	5	150.4		a2	a2	nv		a2	a3	
	4	149.9		a2	a2	nv	a3	a2	a3	
	3	250.9		a2		nv			a3	
	2	379.4		a2		nv		a3	a3	
	1	497.5		a2		nv	a5	a3	a3	
NO ₂ (nmol/mol)	0	0	a2	a2	a2	nv		a2	a3	
	10	13.8		a2	a2	nv		a2	a3	
	8	21.7		a2	a2	nv	a3	a2	a3	
	6	60.5			a2	nv		a2	a3	
	4	102.6		a2	a2	nv		a2	a3	
	2	120.8		a2	a2	nv		a2	a3	

Comparability of NO₂ and ozone measurements via GPT was investigated in studies [26][27], where O₃ was traceable to international standards implementing ultraviolet photometry method and NO₂ was traceable to NO international standards and GPT method was applied, and a significant difference of about 2% was confirmed. At this IE, this difference can not be confirmed by individual participants, due to significant uncertainties attributed to O₃ and NO₂ measurements, but in the general evaluation a difference of 1% is observed between group average NO₂ and average O₃.

8. Conclusions

The proficiency evaluation scheme has provided an assessment of the participants measured values and their evaluated uncertainties. In terms of the criteria imposed by the European Commission (σ_p) 44% of the results reported by AQUILA laboratories fall into 'a1' category and are good both in terms of measured values and evaluated uncertainties. In residual 56% of the results have good measured values but the evaluated uncertainties were either too high, category 'a2' (54%), or too small, category 'a3' (2%). The relative high number of 'a2' cases, where participant's evaluated uncertainty is higher than the common IE criterion, needs further investigation. The common IE criterion is confirmed to be realistic by comparison to reproducibility standard deviation obtained at this (Annex C) and other IEs [25], and is derived from the European standards' uncertainty requirements, which are explicit at high concentrations. Since the uncertainty requirements at zero concentration are not quantitatively stated in the European standards, the IE criteria at zero concentration had to be set within AQUILA. The initially proposed values were in use for IEs since June 2007 to October 2008 but at the November 2008 AQUILA meeting the IE criteria at zero concentration were enlarged and approved. The final values were also communicated to relevant CEN working group for potential future amendments of European standards. With that in mind especially 'a2' results at high concentration levels should be further investigated by the NRLs.

Non of the NRLs have overall unsatisfactory results of the z'-score evaluation (one unsatisfactory, categories 'a6' or 'a7', or two questionable, categories 'a4' or 'a5', result per parameter) which would in the view of AQUILA require participation to the next IE in order to demonstrate remediation measures.

The comparability of results among AQUILA participants is best for O₃ and worst for SO₂ measurement method. The relative reproducibility limits, at the highest studied concentration levels, are 4.8% for NO₂, 7.2% for CO, 3.7% for O₃ and 9.0% for NO which are all below the objective derived from criteria imposed by the European Commission (σ_p). This is not the case for SO₂ where the relative reproducibility limit is 13.2% and the objective is 12.2% and is therefore generally considered as unsatisfactory. For the compound SO₂ further harmonization programmes to improve the comparability among NRLs are needed. Investigations should focus on traceability of gas standards.

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Annex A. Assigned values

The assigned values of tested concentration levels were derived from ERLAPs measurements which are calibrated against the certified reference values of CRMs and are traceable to international standards. In this perspective the assigned values are reference values as defined in the ISO 13528 [18].

ERLAPs SO₂, CO and NO analysers were calibrated according to the methodology described in the ISO 6143 [11]. A different number (4 for SO₂, 7 for CO and 5 for NO) of reference gas mixtures were produced from the primary reference materials (produced and certified by NMi Van Swinden Laboratorium) by dynamic dilution method using mass flow controllers [13]. All flows were measured with a certified volumeter. For the reference gas mixture composition evaluation and for the calibration experiment evaluation two computer applications were used, the “GUM WORKBENCH” [26] and “B-least” [29] respectively. For extending calibration from the NO to NO₂ channel of NO_x analyser the GPT test was performed to establish the efficiency of NO₂-converter. For O₃ measurements, the primary standard was used.

ERLAP’s measurement results were validated by comparison to the group statistics (x^* and s^*) for every parameter and concentration level of the IE. These statistics are calculated from participants, applying the robust method described in the Annex C of the ISO 13528 [18]. The validation is taking in account ERLAP’s measurement result (X) and its standard uncertainty (u_X) as given in expression 6 [18]:

$$\frac{|x^* - X|}{\sqrt{\frac{(1,25 \cdot s^*)^2}{p} + u_X^2}} < 2 \quad (6)$$

Where ‘ x^* ’ and ‘ s^* ’ represent robust average and robust standard deviation respectively and ‘ p ’ is the number of participants.

In Table 6 all inputs for expression 6 are given and all ERLAP’s measurement results are confirmed to be valid.

Table 6: The validation of assigned values (X) by comparison to the robust averages (x*) with taking into the account the standard uncertainties of assigned values (uX'), and robust standard deviations (s*) as denoted by expression 6.

run	unit	X	uX'	x*	s*	val.	run	unit	X	uX'	x*	s*	val.
CO_0	µmol/mol	0.014	0.009	0.004	0.010	OK	NO_0	nmol/mol	0.3	0.4	0.2	0.3	OK
CO_1	µmol/mol	8.503	0.062	8.353	0.163	OK	NO_1	nmol/mol	497.5	5.7	491.4	14.8	OK
CO_2	µmol/mol	5.935	0.044	5.880	0.072	OK	NO_2	nmol/mol	379.4	4.4	378.6	8.5	OK
CO_3	µmol/mol	4.269	0.033	4.233	0.083	OK	NO_3	nmol/mol	250.9	2.9	248.8	6.5	OK
CO_4	µmol/mol	1.975	0.017	1.953	0.046	OK	NO_4	nmol/mol	149.9	1.8	148.9	5.0	OK
CO_5	µmol/mol	0.999	0.011	0.999	0.028	OK	NO_5	nmol/mol	150.4	1.8	148.7	4.6	OK
O3_0	nmol/mol	-0.1	1.1	0.3	0.5	OK	NO_6	nmol/mol	90.1	1.2	90.5	1.0	OK
O3_1	nmol/mol	116.1	1.3	116.0	2.4	OK	NO_7	nmol/mol	51.0	0.8	50.1	2.1	OK
O3_2	nmol/mol	100.0	1.1	100.0	0.7	OK	NO_8	nmol/mol	29.6	0.6	29.5	1.0	OK
O3_3	nmol/mol	59.1	1.1	59.3	0.6	OK	NO_9	nmol/mol	16.1	0.4	15.8	0.6	OK
O3_4	nmol/mol	21.1	1.1	21.2	0.4	OK	NO_10	nmol/mol	2.4	0.4	2.3	0.4	OK
O3_5	nmol/mol	13.7	1.1	14.0	0.4	OK	NO2_0	nmol/mol	0.0	0.2	-0.1	0.4	OK
SO2_0	nmol/mol	0.2	0.3	0.1	0.3	OK	NO2_1	nmol/mol	2.9	0.9	2.5	2.8	OK
SO2_1	nmol/mol	131.1	1.1	132.3	4.2	OK	NO2_2	nmol/mol	120.8	1.7	119.5	1.2	OK
SO2_2	nmol/mol	46.4	0.5	46.6	0.9	OK	NO2_3	nmol/mol	1.3	0.6	1.4	1.6	OK
SO2_3	nmol/mol	18.1	0.3	18.1	0.3	OK	NO2_4	nmol/mol	102.6	1.4	101.6	1.9	OK
SO2_4	nmol/mol	7.7	0.3	7.7	0.2	OK	NO2_5	nmol/mol	0.3	0.5	0.5	1.1	OK
SO2_5	nmol/mol	3.3	0.3	3.2	0.2	OK	NO2_6	nmol/mol	60.5	0.9	59.7	1.2	OK
							NO2_7	nmol/mol	0.1	0.3	0.2	0.6	OK
							NO2_8	nmol/mol	21.7	0.4	20.8	0.6	OK
							NO2_9	nmol/mol	0.1	0.2	0.2	0.4	OK
							NO2_10	nmol/mol	13.8	0.3	13.4	1.0	OK

The homogeneity of test gas was evaluated from measurements at the beginning and end of the distribution line. From the relative differences between beginning and end measurements, average and standard deviation were calculated, and the uncertainty of test gas due to lack of homogeneity was calculated as the sum of squares of these average and standard deviation. The upper and lower limits of bias due to homogeneity was evaluated to be smaller than 0.5% which constitutes the relative standard uncertainty of 0,3% of tested concentration level. The standard uncertainties of assigned/reference values (u_X) were calculated with equation 7 and used in the proficiency evaluations of chapter 5.

$$u_X^2 = u_{X'}^2 + (X \cdot u_{\text{homogeneity}})^2 \quad (7)$$

Annex B. The results of the IE

The reported values, presented also in graphs, are given in this annex. The participants were asked to report results (x_{ij} , $u(x_i)$ and $U(x_i)$) expressed in mol/mol units. For all the runs except concentration levels 0, also average (\bar{x}_i) and standard deviation (s_i) of each participant are presented. As a group evaluation robust average (x^*) and robust standard deviation (s^*) were calculated (applying the procedure described in Annex C of ISO 13528) for each run, and are presented in the following tables. The assigned value is indicated on the graphs with the red line and the individual laboratories expanded uncertainties ($U(x_i)$) are indicated with error bars.

Reported values for SO₂

Table 7: Reported values for SO₂ concentration level 0.

parameter: SO2		all units are nmol/mol					
level: 0		x*: 0.08 s*: 0.21					
	A	B	C	E	G	H	
$x_{i,1}$	0.12	0.00	0.62	0.23	0.0	-0.19	
$u(x_i)$	0.50	1.0	1.52	0.21			
$U(x_i)$	1.00	2.0	3.03	0.42			

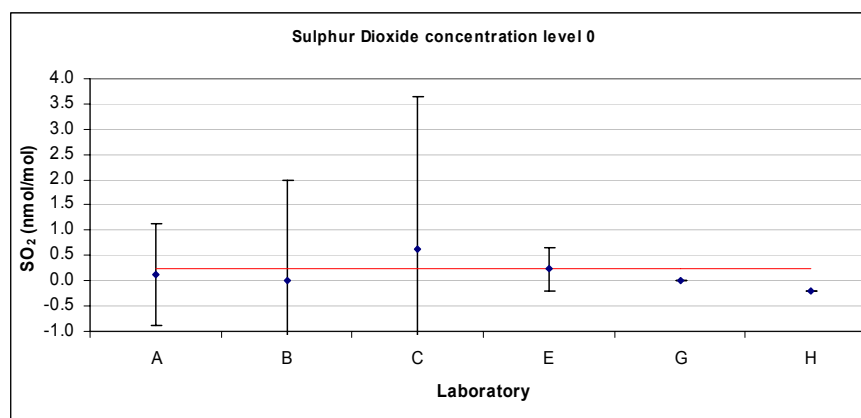


Figure 13: Reported values for SO₂ concentration level 0.

Table 8: Reported values for SO₂ concentration level 1.

parameter: SO2		all units are nmol/mol					
level: 1		x*: 132.25			s*: 4.15		
	A	B	C	E	G	H	
xi,1	130.88	136.10	126.94	131.04	139.1	131.43	
xi,2	130.91	136.50	127.20	131.05	139.5	131.60	
xi,3	130.79	136.50	126.98	131.06	140.0	131.76	
xi	130.860	136.367	127.040	131.050	139.53	131.597	
si	0.062	0.231	0.140	0.010	0.45	0.165	
u(xi)	4.65	3.9	4.68	0.94			
U(xi)	9.30	7.7	9.35	1.88			

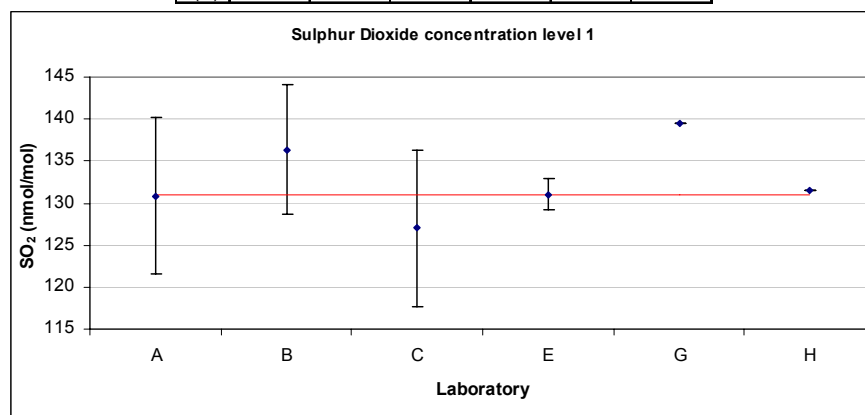


Figure 14: Reported values for SO₂ concentration level 1.

Table 9: Reported values for SO₂ concentration level 2.

parameter: SO2		all units are nmol/mol					
level: 2		x*: 46.57			s*: 0.86		
	A	B	C	E	G	H	
xi,1	46.54	48.50	45.41	46.38	49.6	46.45	
xi,2	46.43	48.32	45.46	46.41	49.6	46.30	
xi,3	46.03	48.30	45.51	46.40	49.7	46.29	
xi	46.333	48.373	45.460	46.397	49.63	46.347	
si	0.268	0.110	0.050	0.015	0.06	0.090	
u(xi)	1.64	1.4	2.64	0.41			
U(xi)	3.29	2.8	5.27	0.82			

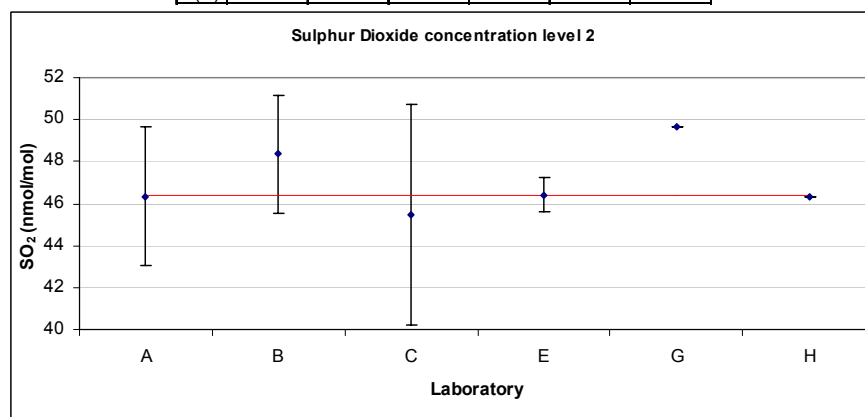


Figure 15: Reported values for SO₂ concentration level 2.

Table 10: Reported values for SO₂ concentration level 3.

parameter: SO ₂		all units are nmol/mol					
level: 3		x*: 18.13			s*: 0.29		
	A	B	C	E	G	H	
xi,1	17.77	18.72	18.00	18.06	19.2	17.84	
xi,2	17.88	18.55	18.10	18.06	19.2	17.91	
xi,3	18.01	18.61	18.06	18.05	19.2	17.89	
xi	17.887	18.627	18.053	18.057	19.20	17.880	
si	0.120	0.086	0.050	0.006	0.00	0.036	
u(xi)	0.63	1.0	1.95	0.27			
U(xi)	1.27	2.0	3.90	0.54			

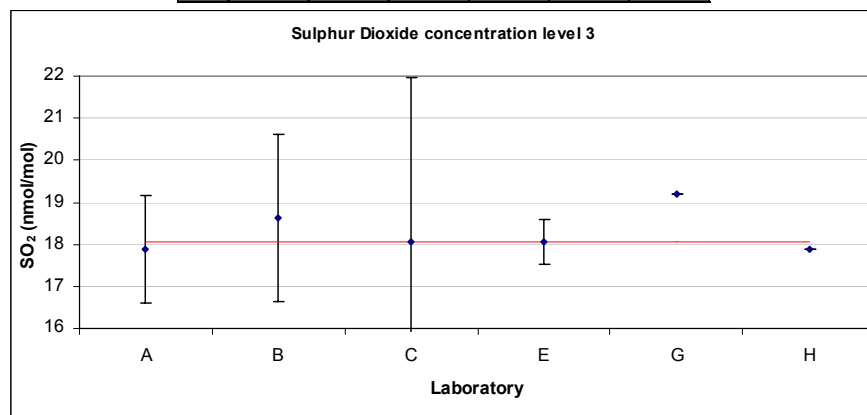


Figure 16: Reported values for SO₂ concentration level 3.

Table 11: Reported values for SO₂ concentration level 4.

parameter: SO ₂		all units are nmol/mol					
level: 4		x*: 7.71			s*: 0.16		
	A	B	C	E	G	H	
xi,1	7.76	7.56	7.89	7.66	7.9	7.44	
xi,2	7.64	7.72	7.91	7.67	7.8	7.36	
xi,3	7.65	7.83	7.92	7.63	7.8	7.38	
xi	7.683	7.703	7.907	7.653	7.83	7.393	
si	0.067	0.136	0.015	0.021	0.06	0.042	
u(xi)	0.27	1.0	1.70	0.23			
U(xi)	0.54	2.0	3.40	0.46			

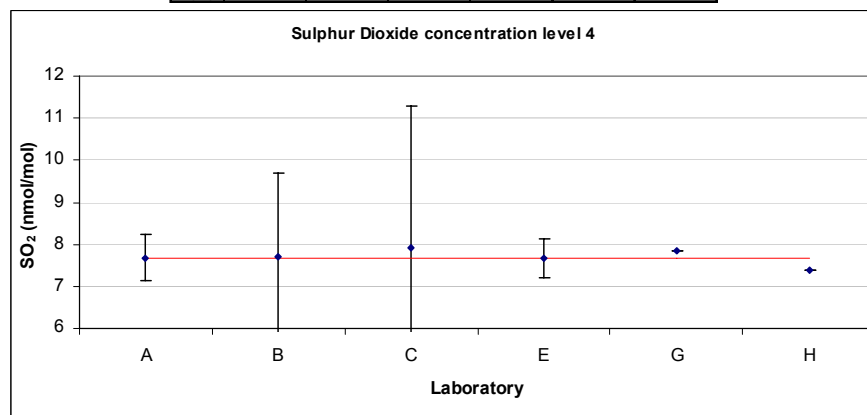


Figure 17: Reported values for SO₂ concentration level 4.

Table 12: Reported values for SO₂ concentration level 5.

parameter: SO2		all units are nmol/mol					
level: 5		x*: 3.20			s*: 0.18		
	A	B	C	E	G	H	
xi,1	3.26	3.10	3.48	3.26	3.3	2.94	
xi,2	3.06	3.11	3.45	3.24	3.2	2.92	
xi,3	3.34	2.95	3.41	3.25	3.2	2.88	
xi	3.220	3.053	3.447	3.250	3.23	2.913	
si	0.144	0.090	0.035	0.010	0.06	0.031	
u(xi)	0.11	1.0	1.59	0.22			
U(xi)	0.23	2.0	3.17	0.44			

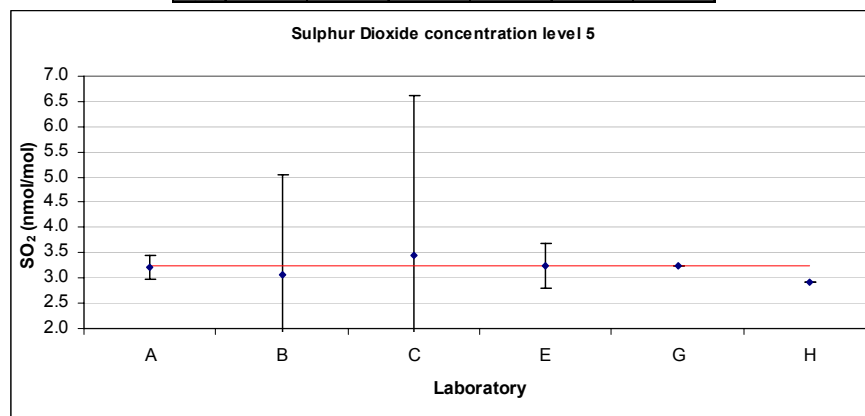


Figure 18: Reported values for SO₂ concentration level 5.

Reported values for CO

Table 13: Reported values for CO concentration level 0.

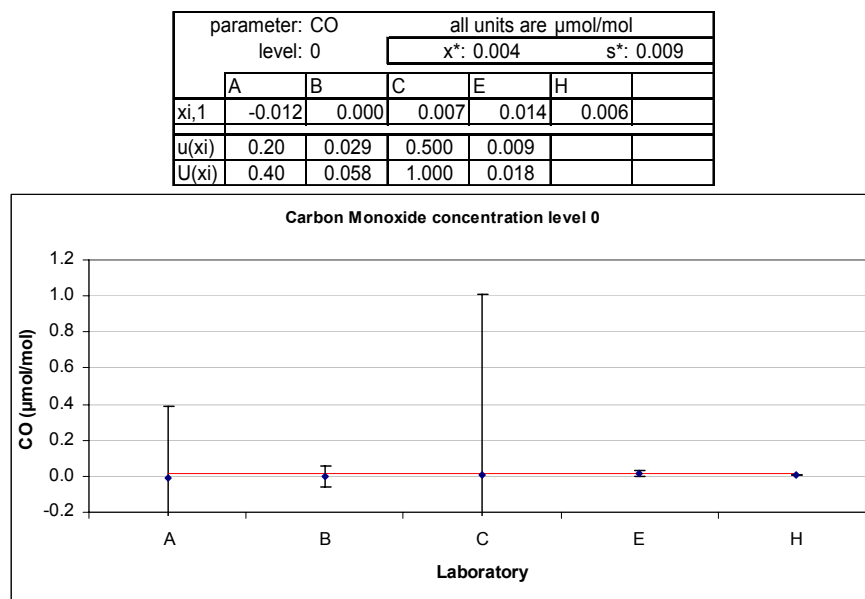


Figure 19: Reported values for CO concentration level 0.

Table 14: Reported values for CO concentration level 1.

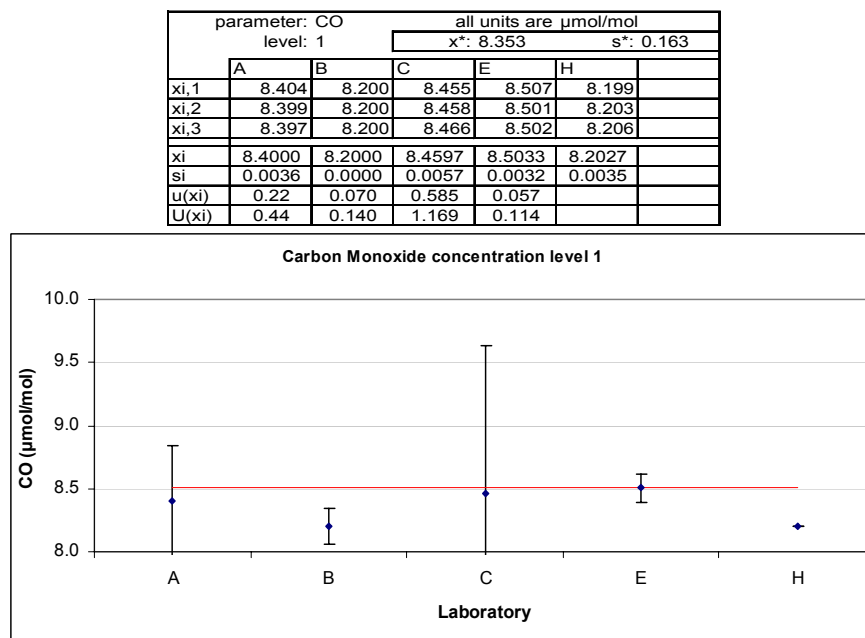


Figure 20: Reported values for CO concentration level 1.

Table 15: Reported values for CO concentration level 2.

parameter: CO level: 2		all units are $\mu\text{mol/mol}$				
		x^* : 5.880			s^* : 0.072	
	A	B	C	E	H	
$x_{i,1}$	5.938	5.700	5.898	5.935	5.757	
$x_{i,2}$	5.939	5.750	5.900	5.936	5.755	
$x_{i,3}$	5.940	5.800	5.901	5.935	5.759	
\bar{x}_i	5.9390	5.7500	5.8997	5.9353	5.7570	
s_i	0.0010	0.0500	0.0015	0.0006	0.0020	
$u(x_i)$	0.15	0.060	0.559	0.040		
$U(x_i)$	0.31	0.120	1.118	0.080		

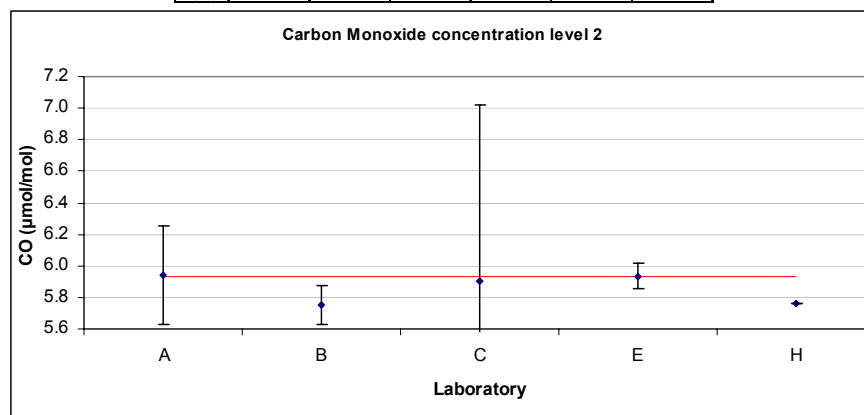


Figure 21: Reported values for CO concentration level 2.

Table 16: Reported values for CO concentration level 3.

parameter: CO level: 3		all units are $\mu\text{mol/mol}$				
		x^* : 4.233			s^* : 0.083	
	A	B	C	E	H	
$x_{i,1}$	4.334	4.100	4.239	4.266	4.158	
$x_{i,2}$	4.333	4.200	4.239	4.268	4.159	
$x_{i,3}$	4.334	4.200	4.239	4.272	4.160	
\bar{x}_i	4.3337	4.1667	4.2390	4.2687	4.1590	
s_i	0.0006	0.0577	0.0000	0.0031	0.0010	
$u(x_i)$	0.11	0.060	0.542	0.030		
$U(x_i)$	0.23	0.110	1.085	0.060		

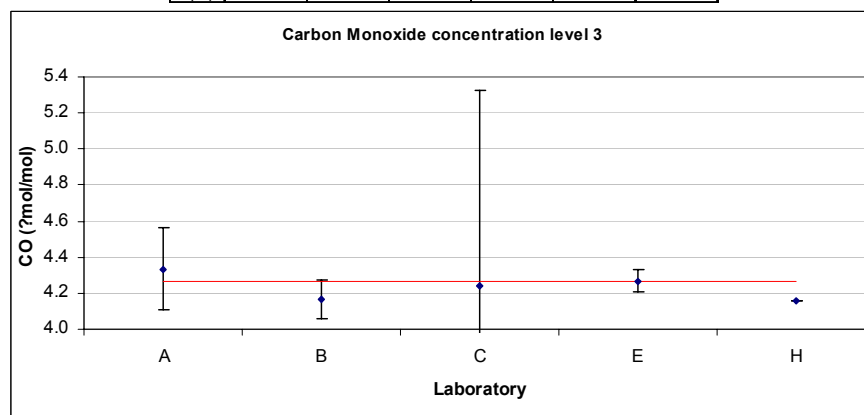


Figure 22: Reported values for CO concentration level 3.

Table 17: Reported values for CO concentration level 4.

parameter: CO		all units are $\mu\text{mol/mol}$				
level: 4		x*: 1.953 s*: 0.046				
	A	B	C	E	H	
xi,1	2.098	1.900	1.950	1.972	1.932	
xi,2	2.089	1.900	1.949	1.977	1.932	
xi,3	2.085	1.900	1.952	1.977	1.933	
xi	2.0907	1.9000	1.9503	1.9753	1.9323	
si	0.0067	0.0000	0.0015	0.0029	0.0006	
u(xi)	0.05	0.032	0.520	0.016		
U(xi)	0.11	0.064	1.039	0.032		

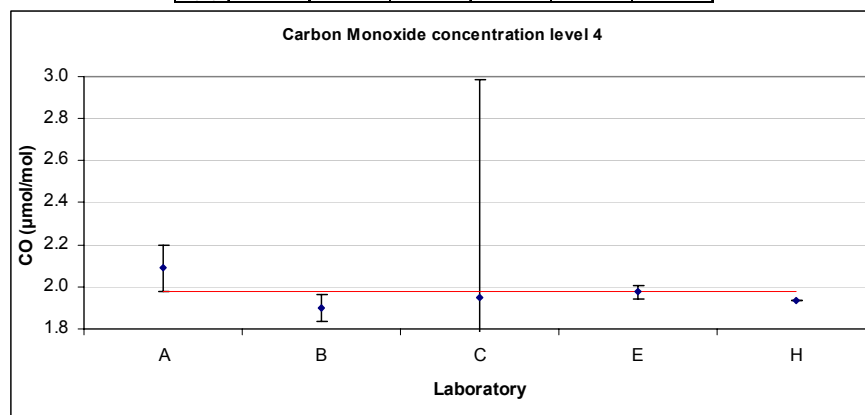


Figure 23: Reported values for CO concentration level 4.

Table 18: Reported values for CO concentration level 5.

parameter: CO		all units are $\mu\text{mol/mol}$				
level: 5		x*: 0.999 s*: 0.028				
	A	B	C	E	H	
xi,1	1.049	1.000	0.979	0.997	0.976	
xi,2	1.046	1.000	0.983	0.999	0.976	
xi,3	1.047	1.000	0.980	1.000	0.976	
xi	1.0473	1.0000	0.9807	0.9987	0.9760	
si	0.0015	0.0000	0.0021	0.0015	0.0000	
u(xi)	0.03	0.030	0.510	0.011		
U(xi)	0.05	0.060	1.020	0.022		

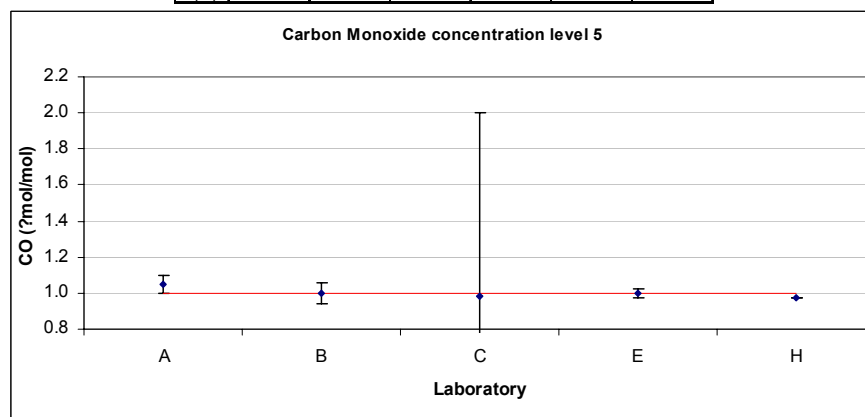


Figure 24: Reported values for CO concentration level 5.

Reported values for O₃

Table 19: Reported values for O₃ concentration level 0.

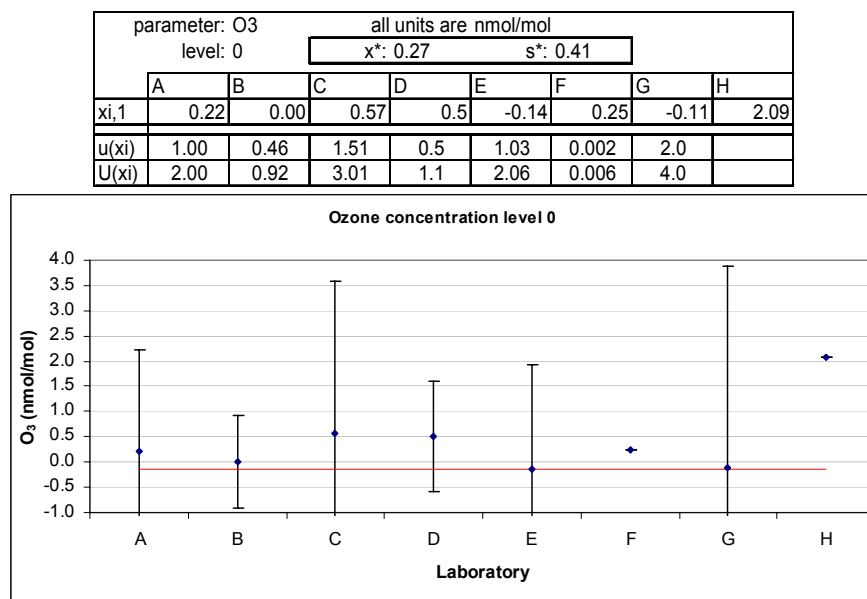


Figure 25: Reported values for O₃ concentration level 0.

Table 20: Reported values for O₃ concentration level 1.

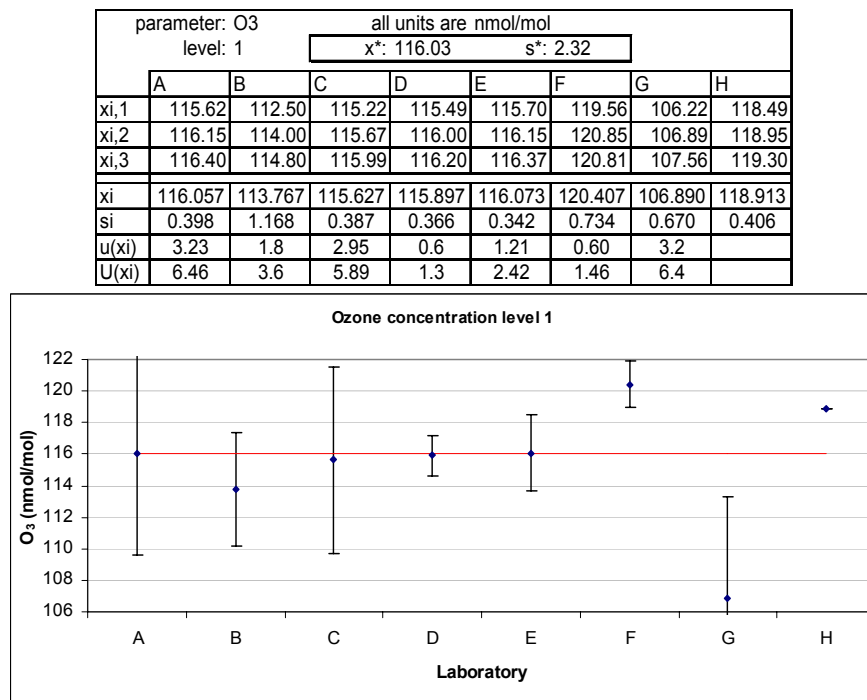


Figure 26: Reported values for O₃ concentration level 1.

Table 21: Reported values for O₃ concentration level 2.

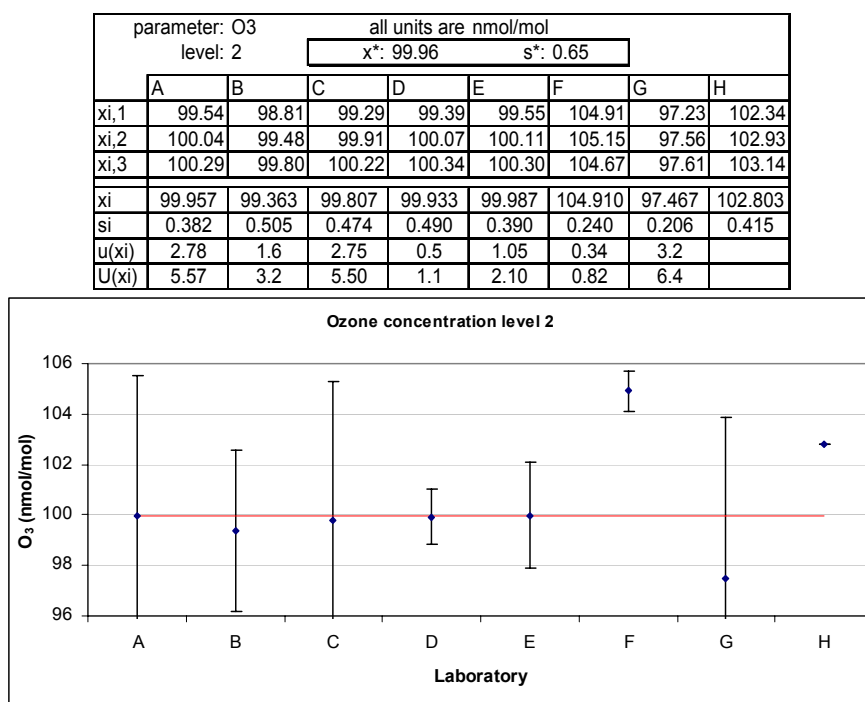


Figure 27: Reported values for O₃ concentration level 2.

Table 22: Reported values for O₃ concentration level 3.

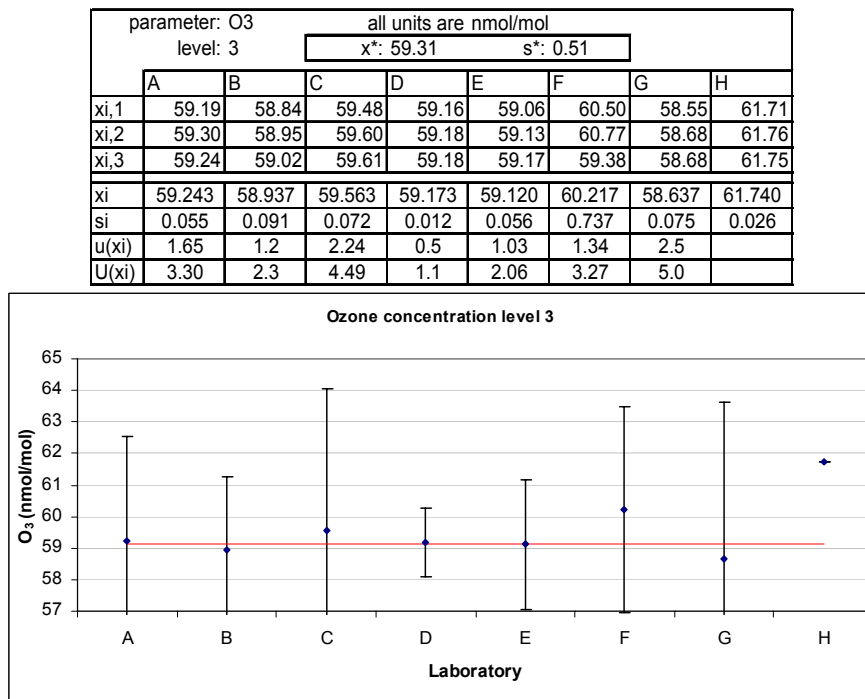


Figure 28: Reported values for O₃ concentration level 3.

Table 23: Reported values for O₃ concentration level 4.

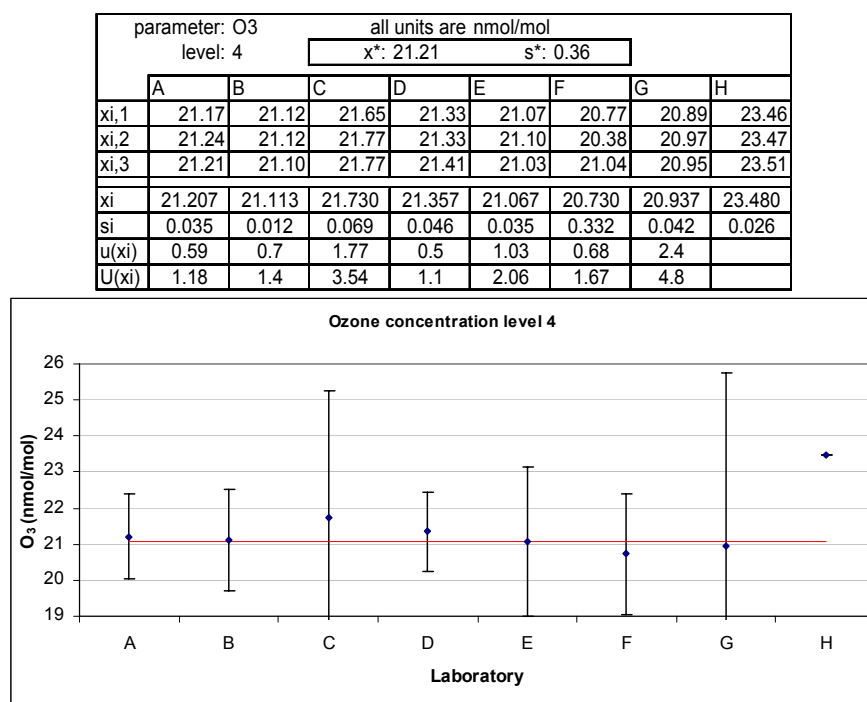


Figure 29: Reported values for O₃ concentration level 4.

Table 24: Reported values for O₃ concentration level 5.

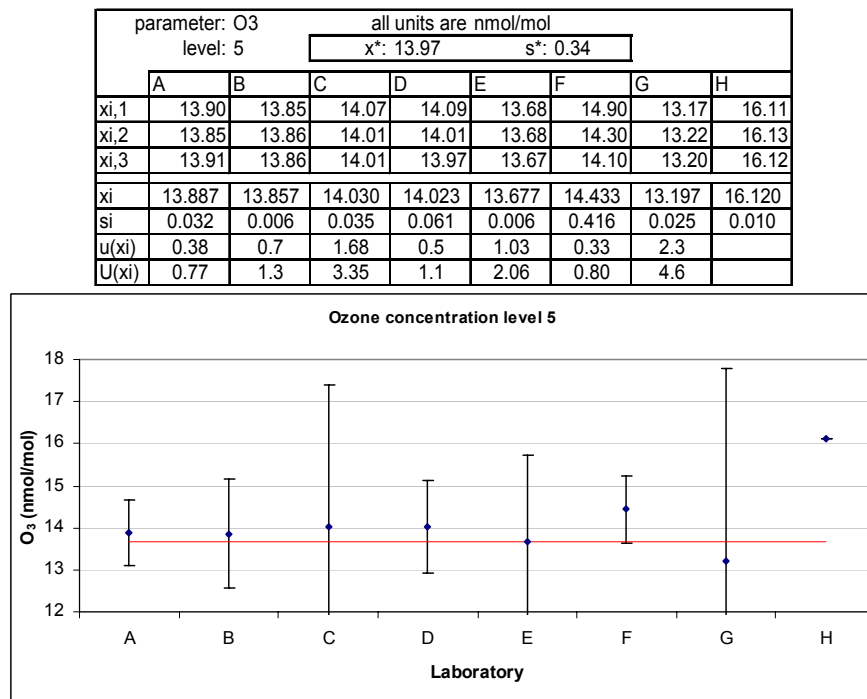


Figure 30: Reported values for O₃ concentration level 5.

Reported values for NO

Table 25: Reported values for NO concentration level 0.

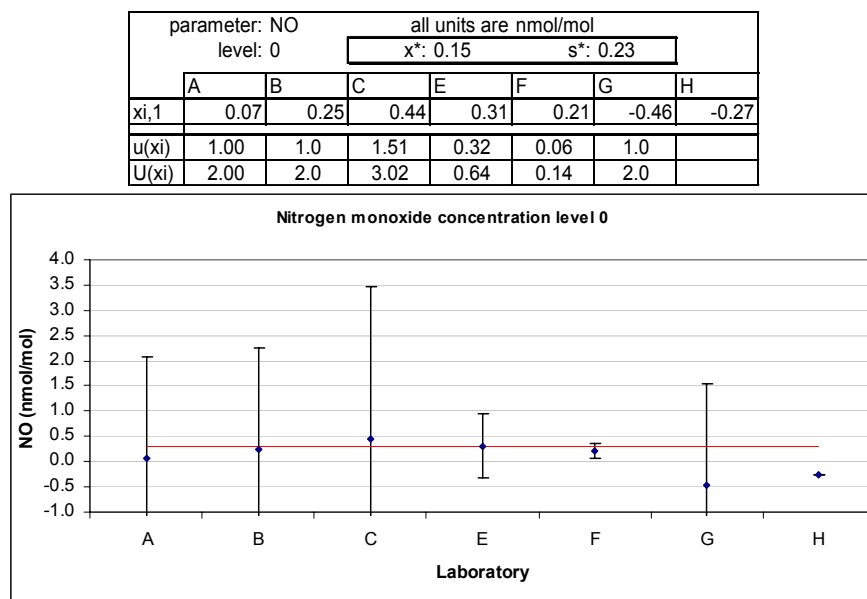


Figure 31: Reported values for NO concentration level 0.

Table 26: Reported values for NO concentration level 1.

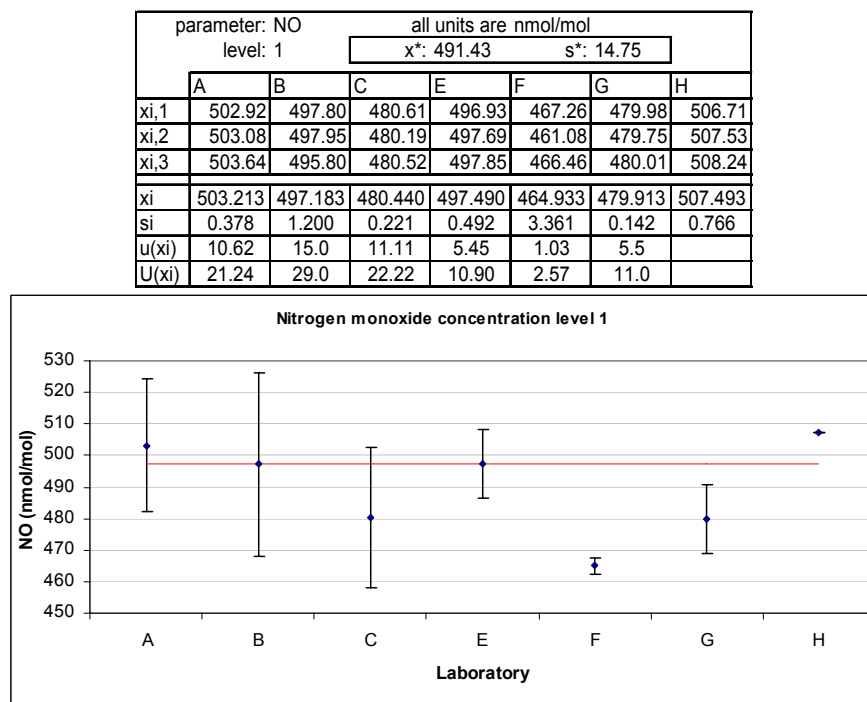


Figure 32: Reported values for NO concentration level 1.

Table 27: Reported values for NO concentration level 2.

parameter: NO		all units are nmol/mol					
level: 2		x*: 378.56		s*: 8.42			
	A	B	C	E	F	G	H
xi,1	387.27	375.50	373.70	379.44	379.73	364.75	388.51
xi,2	386.07	375.80	373.65	379.54	380.05	364.80	388.52
xi,3	386.34	375.85	373.69	379.20	377.94	365.20	388.25
xi	386.560	375.717	373.680	379.393	379.240	364.917	388.427
si	0.630	0.189	0.026	0.175	1.137	0.247	0.153
u(xi)	8.16	11.0	8.97	4.17	0.99	5.1	
U(xi)	16.32	22.0	17.95	8.34	2.42	10.2	

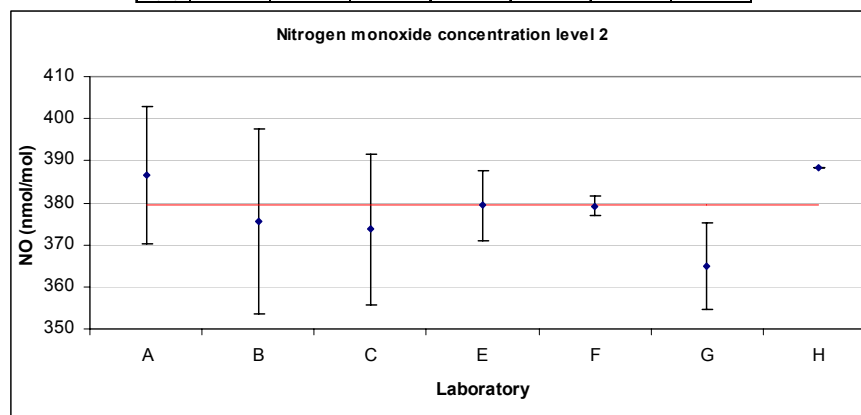


Figure 33: Reported values for NO concentration level 2.

Table 28: Reported values for NO concentration level 3.

parameter: NO		all units are nmol/mol					
level: 3		x*: 248.79		s*: 6.48			
	A	B	C	E	F	G	H
xi,1	253.87	243.75	244.19	250.69	249.20	241.65	257.11
xi,2	253.63	244.80	244.42	250.98	248.37	241.64	257.81
xi,3	254.22	245.00	244.43	251.11	248.22	241.79	257.72
xi	253.907	244.517	244.347	250.927	248.597	241.693	257.547
si	0.297	0.671	0.136	0.215	0.528	0.084	0.381
u(xi)	5.36	7.3	6.39	2.79	0.37	5.1	
U(xi)	10.72	14.5	12.77	5.58	0.89	10.2	

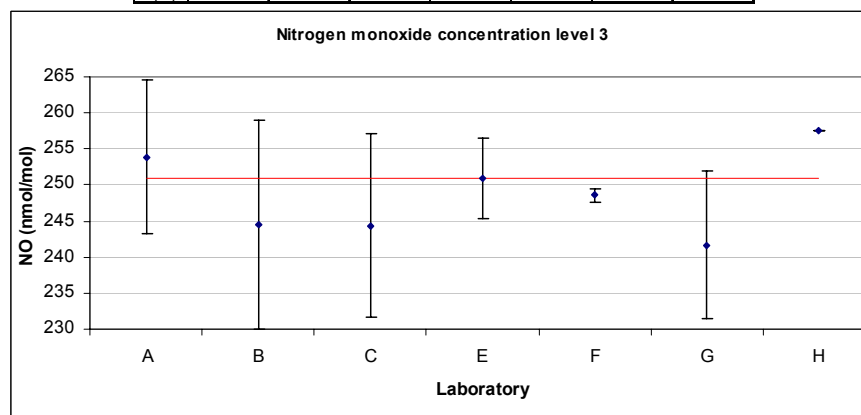


Figure 34: Reported values for NO concentration level 3.

Table 29: Reported values for NO concentration level 4.

parameter: NO		all units are nmol/mol					
level: 4		x*: 148.86		s*: 4.96			
	A	B	C	E	F	G	H
xi,1	152.38	146.15	151.69	149.99	143.38	142.85	154.44
xi,2	153.24	146.45	151.65	149.90	145.82	142.89	154.23
xi,3	152.40	146.35	151.36	149.94	144.10	142.74	154.20
xi	152.673	146.317	151.567	149.943	144.433	142.827	154.290
si	0.491	0.153	0.180	0.045	1.254	0.078	0.131
u(xi)	3.22	4.3	4.53	1.71	0.73	5.1	
U(xi)	6.44	8.4	9.06	3.42	1.78	10.2	

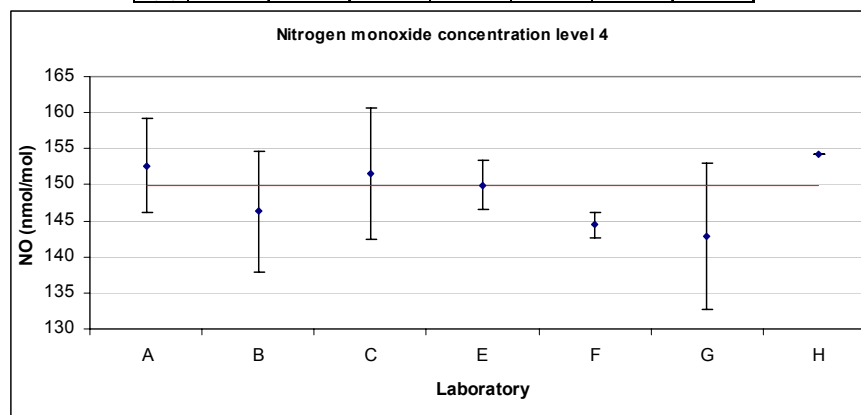


Figure 35: Reported values for NO concentration level 4.

Table 30: Reported values for NO concentration level 5.

parameter: NO		all units are nmol/mol					
level: 5		x*: 148.70		s*: 4.51			
	A	B	C	E	F	G	H
xi,1	150.95	143.55	146.82	150.38	149.10	143.74	154.56
xi,2	150.79	144.15	146.88	150.44	150.24	143.81	154.62
xi,3	150.84	144.55	146.93	150.33	151.92	143.56	154.58
xi	150.860	144.083	146.877	150.383	150.420	143.703	154.587
si	0.082	0.503	0.055	0.055	1.419	0.129	0.031
u(xi)	3.18	4.4	4.44	1.72	0.36	5.1	
U(xi)	6.37	8.7	8.88	3.44	0.89	10.2	

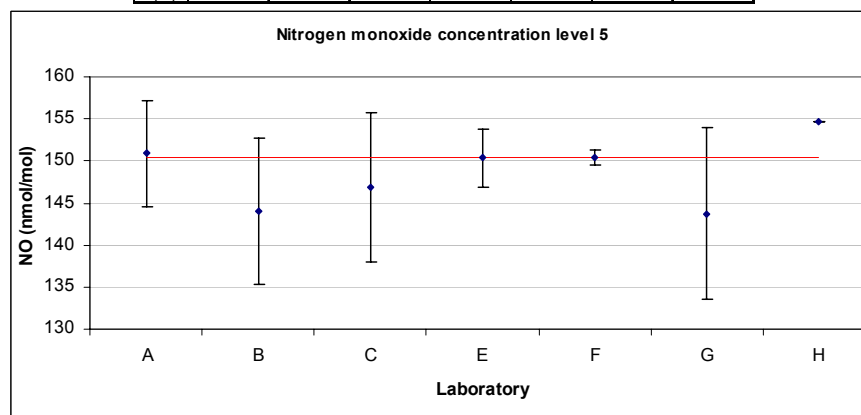


Figure 36: Reported values for NO concentration level 5.

Table 31: Reported values for NO concentration level 6.

parameter: NO level: 6		all units are nmol/mol					
		x*: 90.54			s*: 1.00		
	A	B	C	E	F	G	H
xi,1	90.74	85.60	91.07	89.98	91.26	85.09	92.57
xi,2	91.21	85.80	91.19	90.14	90.26	85.40	92.74
xi,3	91.37	85.80	91.18	90.24	90.37	85.25	92.71
xi	91.107	85.733	91.147	90.120	90.630	85.247	92.673
si	0.327	0.115	0.067	0.131	0.548	0.155	0.091
u(xi)	1.92	2.6	3.32	1.08	0.57	4.1	
U(xi)	3.85	6.2	6.65	2.16	1.46	8.2	

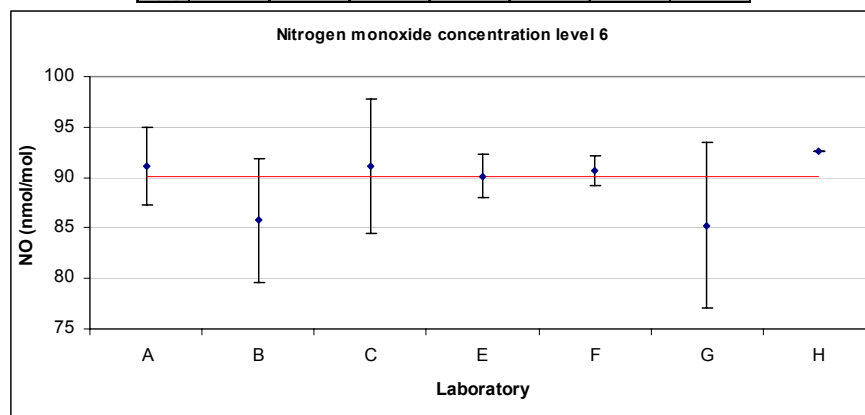


Figure 37: Reported values for NO concentration level 6.

Table 32: Reported values for NO concentration level 7.

parameter: NO level: 7		all units are nmol/mol					
		x*: 50.15			s*: 2.07		
	A	B	C	E	F	G	H
xi,1	50.18	47.65	49.71	50.90	51.82	48.08	52.22
xi,2	50.48	47.55	49.69	50.99	51.85	48.15	52.34
xi,3	50.38	47.55	49.68	51.00	52.44	48.05	52.39
xi	50.347	47.583	49.693	50.963	52.037	48.093	52.317
si	0.153	0.058	0.015	0.055	0.350	0.051	0.087
u(xi)	1.06	1.5	2.49	0.69	0.69	3.5	
U(xi)	2.12	2.9	4.99	1.38	1.68	7.0	

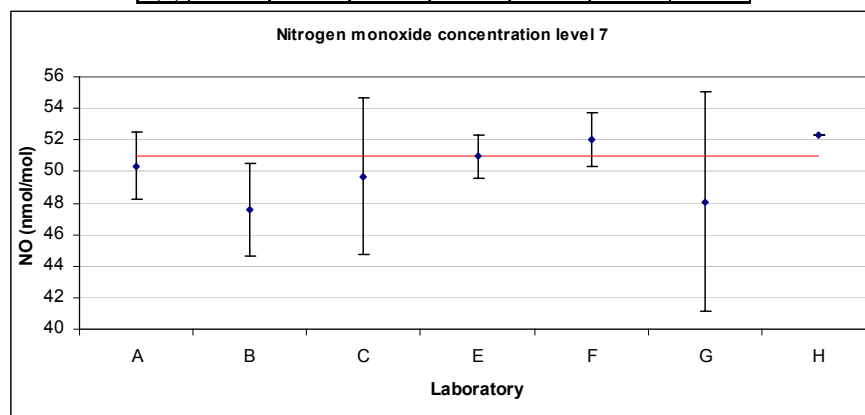


Figure 38: Reported values for NO concentration level 7.

Table 33: Reported values for NO concentration level 8.

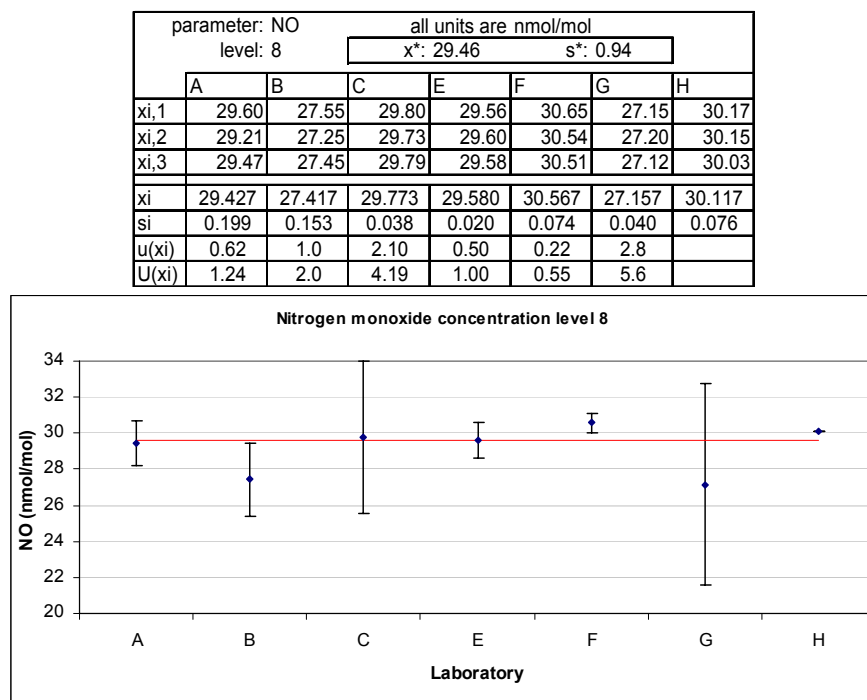


Figure 39: Reported values for NO concentration level 8.

Table 34: Reported values for NO concentration level 9.

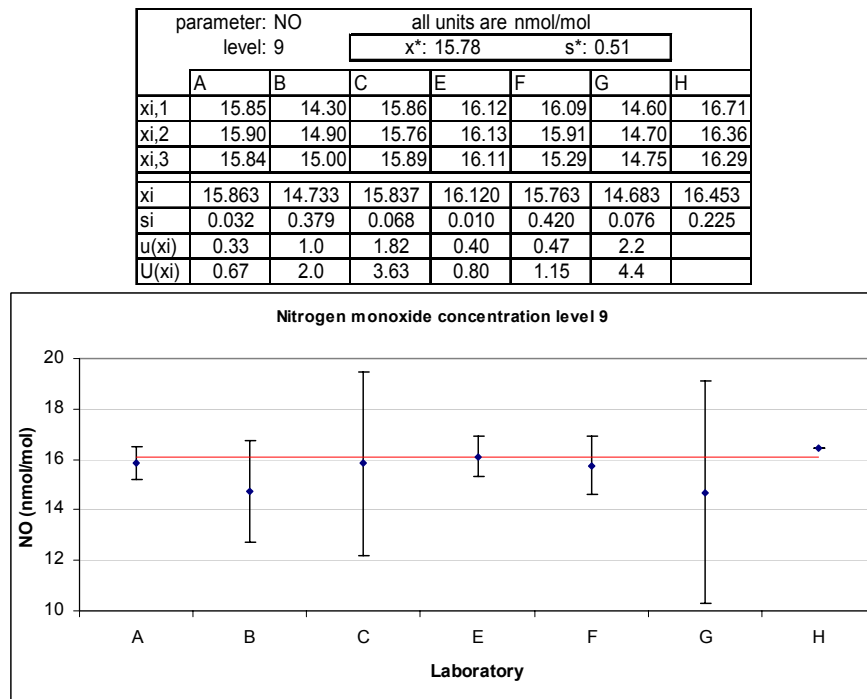


Figure 40: Reported values for NO concentration level 9.

Table 35: Reported values for NO concentration level 10.

parameter: NO level: 10		all units are nmol/mol					
		x*: 2.31			s*: 0.31		
	A	B	C	E	F	G	H
xi,1	2.49	2.45	3.03	2.42	2.57	1.33	2.02
xi,2	2.53	2.00	3.01	2.39	2.13	1.28	1.93
xi,3	2.41	2.15	3.03	2.36	2.42	1.34	1.81
xi	2.477	2.200	3.023	2.390	2.373	1.317	1.920
si	0.061	0.229	0.012	0.030	0.224	0.032	0.105
u(xi)	0.21	1.0	1.56	0.33	0.15	1.1	
U(xi)	0.42	2.0	3.12	0.66	0.36	2.2	

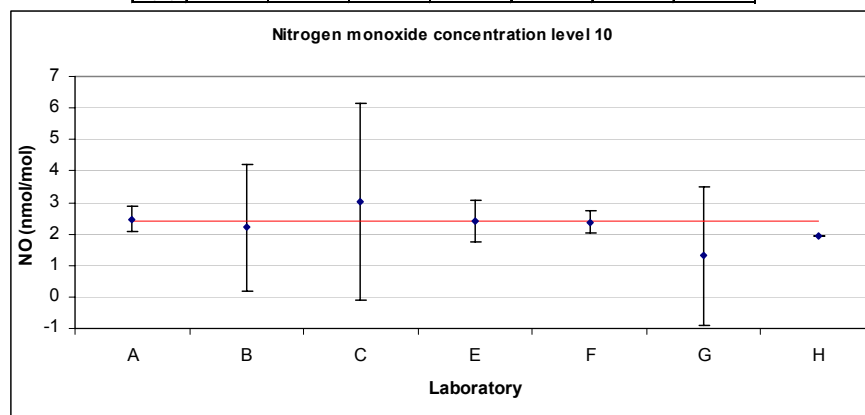


Figure 41: Reported values for NO concentration level 10.

Reported values for NO₂

Table 36: Reported values for NO₂ concentration level 0.

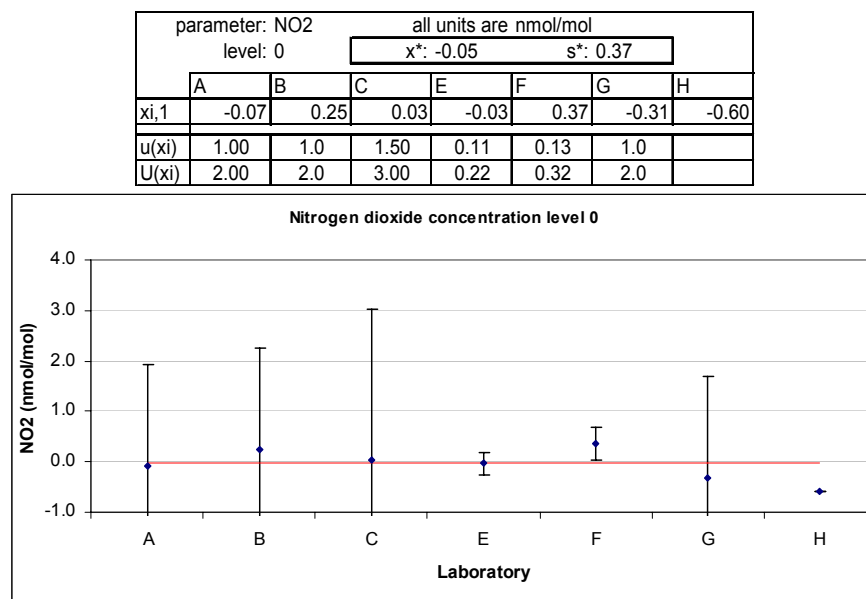


Figure 42: Reported values for NO₂ concentration level 0.

Table 37: Reported values for NO₂ concentration level 1.

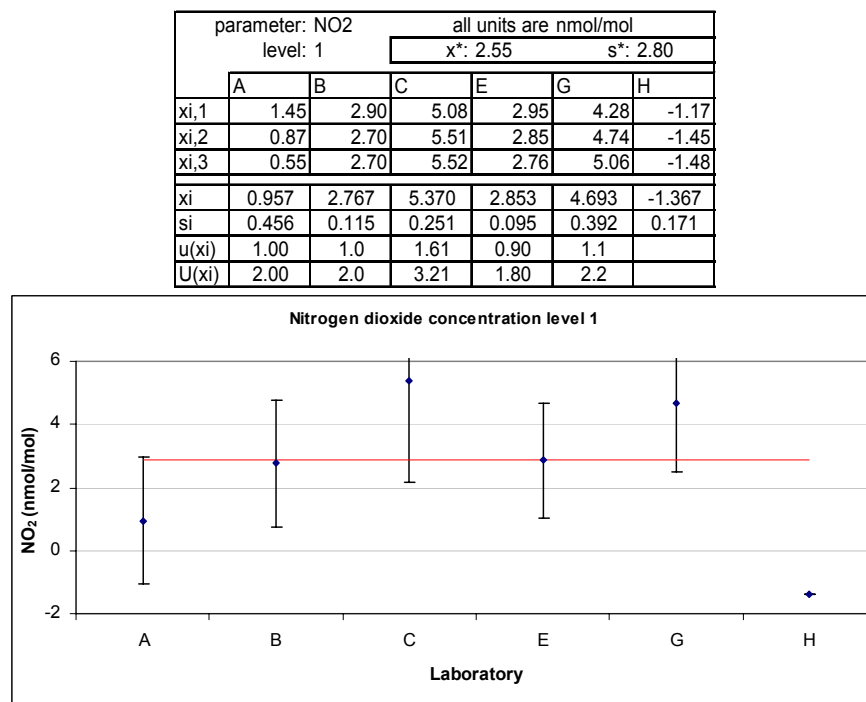


Figure 43: Reported values for NO₂ concentration level 1.

Table 38: Reported values for NO₂ concentration level 2.

parameter: NO2		all units are nmol/mol					
level: 2		x*: 119.53		s*: 1.18			
	A	B	C	E	F	G	H
xi,1	118.05	121.10	119.15	120.82	120.75	117.94	119.08
xi,2	119.17	120.75	119.06	120.75	120.65	118.43	119.15
xi,3	117.85	120.60	119.10	120.71	118.87	118.73	119.51
xi	118.357	120.817	119.103	120.760	120.090	118.367	119.247
si	0.711	0.257	0.045	0.056	1.058	0.399	0.231
u(xi)	2.50	3.5	3.88	1.65	0.31	4.5	
U(xi)	5.00	7.0	7.76	3.30	0.76	9.0	

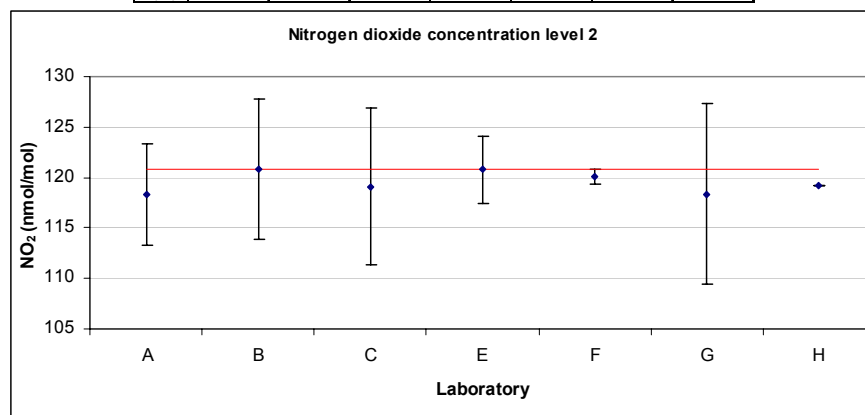


Figure 44: Reported values for NO₂ concentration level 2.

Table 39: Reported values for NO₂ concentration level 3.

parameter: NO2		all units are nmol/mol					
level: 3		x*: 1.40		s*: 1.60			
	A	B	C	E	G	H	
xi,1	0.47	2.10	2.95	1.33	2.46	-0.79	
xi,2	0.05	2.60	2.88	1.31	2.52	-1.09	
xi,3	0.07	1.65	3.06	1.12	2.56	-1.09	
xi	0.197	2.117	2.963	1.253	2.513	-0.990	
si	0.237	0.475	0.091	0.116	0.050	0.173	
u(xi)	1.00	1.0	1.56	0.53	1.1		
U(xi)	2.00	2.0	3.12	1.06	2.2		

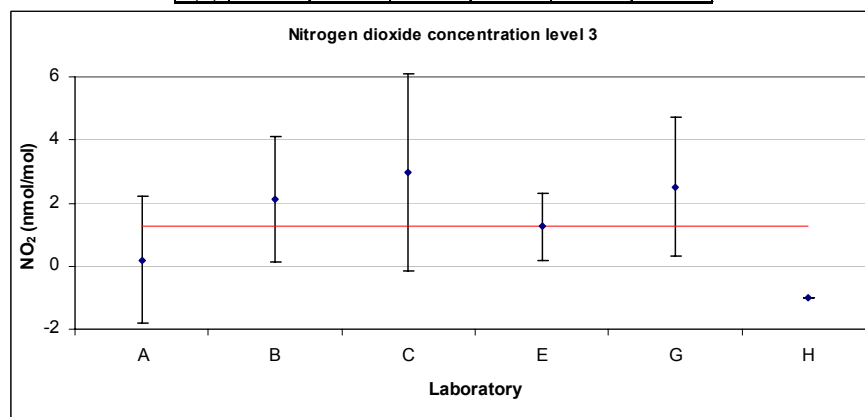


Figure 45: Reported values for NO₂ concentration level 3.

Table 40: Reported values for NO₂ concentration level 4.

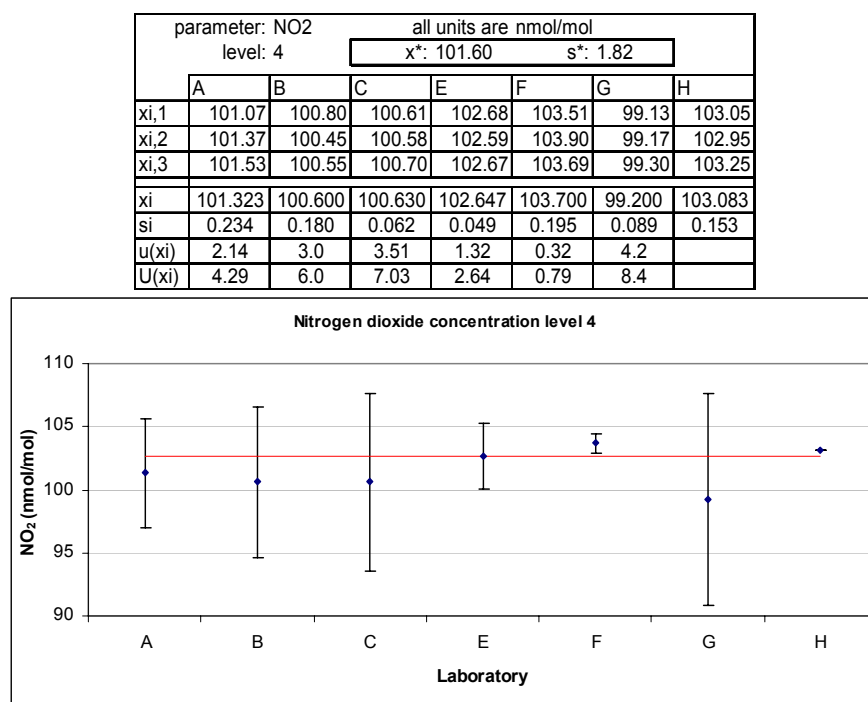


Figure 46: Reported values for NO₂ concentration level 4.

Table 41: Reported values for NO₂ concentration level 5.

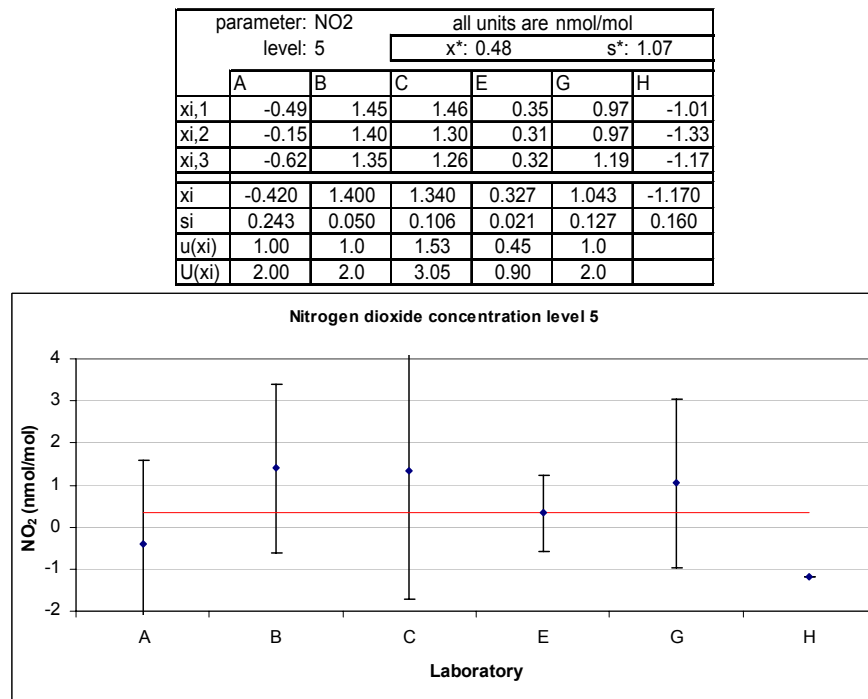


Figure 47: Reported values for NO₂ concentration level 5.

Table 42: Reported values for NO₂ concentration level 6.

parameter: NO2 level: 6		all units are nmol/mol					
		x*: 59.70			s*: 1.18		
	A	B	C	E	F	G	H
xi,1	59.70	59.00	59.29	60.77	61.91	58.31	61.22
xi,2	59.08	59.10	59.10	60.49	60.35	58.22	61.04
xi,3	58.96	59.20	58.86	60.35	59.50	58.14	61.00
xi	59.247	59.100	59.083	60.537	60.587	58.223	61.087
si	0.397	0.100	0.215	0.214	1.222	0.085	0.117
u(xi)	1.25	1.8	2.68	0.82	0.45	3.9	
U(xi)	2.50	3.5	5.36	1.64	1.13	7.8	

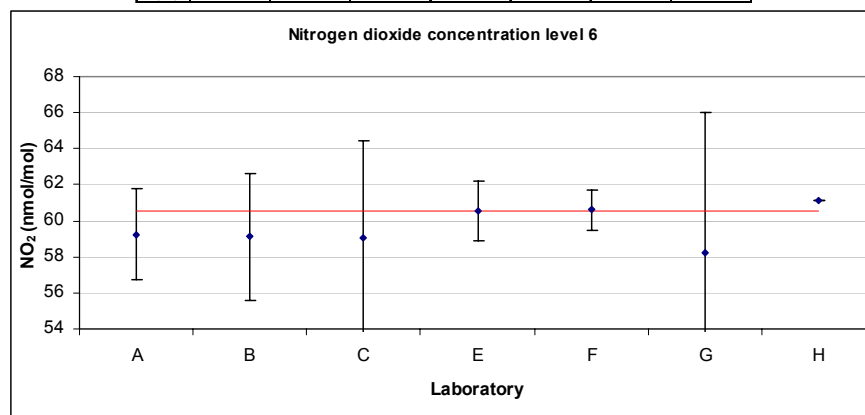


Figure 48: Reported values for NO₂ concentration level 6.

Table 43: Reported values for NO₂ concentration level 7.

parameter: NO2 level: 7		all units are nmol/mol					
		x*: 0.19			s*: 0.50		
	A	B	C	E	G	H	
xi,1	-0.36	0.85	0.61	0.22	0.11	-0.23	
xi,2	-0.18	0.85	0.41	0.10	0.01	-0.20	
xi,3	-0.26	1.00	0.44	0.11	0.16	-0.24	
xi	-0.267	0.900	0.487	0.143	0.093	-0.223	
si	0.090	0.087	0.108	0.067	0.076	0.021	
u(xi)	1.00	1.0	1.51	0.25	1.0		
U(xi)	2.00	2.0	3.02	0.50	2.0		

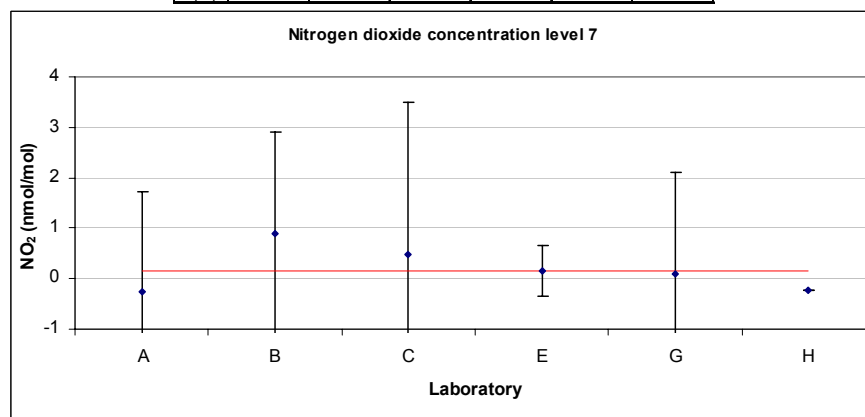


Figure 49: Reported values for NO₂ concentration level 7.

Table 44: Reported values for NO₂ concentration level 8.

parameter: NO2		all units are nmol/mol					
level: 8		x*: 20.83		s*: 0.54			
	A	B	C	E	F	G	H
xi,1	20.78	20.55	20.68	21.69	19.46	20.51	22.07
xi,2	20.80	21.05	20.53	21.67	19.62	20.52	22.03
xi,3	20.81	21.10	20.57	21.70	20.77	20.50	22.17
xi	20.797	20.900	20.593	21.687	19.950	20.510	22.090
si	0.015	0.304	0.078	0.015	0.715	0.010	0.072
u(xi)	0.44	1.0	1.91	0.36	0.32	2.9	
U(xi)	0.88	2.0	3.82	0.72	0.78	5.8	

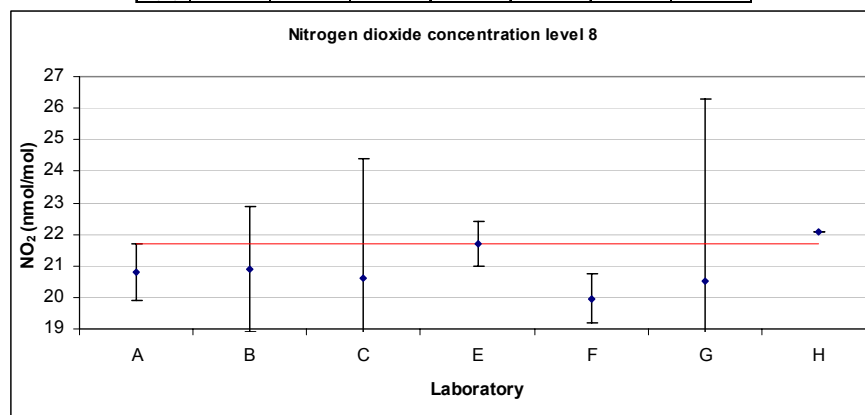


Figure 50: Reported values for NO₂ concentration level 8.

Table 45: Reported values for NO₂ concentration level 9.

parameter: NO2		all units are nmol/mol					
level: 9		x*: 0.18		s*: 0.36			
	A	B	C	E	G	H	
xi,1	-0.22	0.75	0.39	0.08	-0.13	0.25	
xi,2	-0.12	0.55	0.46	0.10	-0.15	0.26	
xi,3	-0.13	0.65	0.39	0.09	-0.15	0.21	
xi	-0.157	0.650	0.413	0.090	-0.143	0.240	
si	0.055	0.100	0.040	0.010	0.012	0.026	
u(xi)	1.00	1.0	1.51	0.18	1.0		
U(xi)	2.00	2.0	3.02	0.36	2.0		

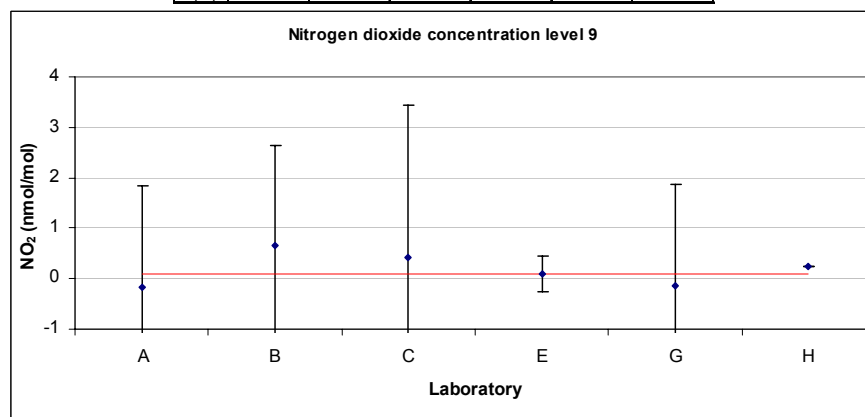


Figure 51: Reported values for NO₂ concentration level 9.

Table 46: Reported values for NO₂ concentration level 10.

parameter: NO2		all units are nmol/mol					
level: 10		x*: 13.44			s*: 0.93		
	A	B	C	E	F	G	H
xi,1	12.92	12.70	13.13	13.74	14.56	12.88	14.33
xi,2	13.35	12.15	13.14	13.79	14.46	12.85	14.41
xi,3	13.20	12.00	13.05	13.78	14.78	12.87	14.45
xi	13.157	12.283	13.107	13.770	14.600	12.867	14.397
si	0.218	0.369	0.049	0.026	0.164	0.015	0.061
u(xi)	0.28	1.0	1.76	0.23	0.39	2.6	
U(xi)	0.55	2.0	3.52	0.46	0.95	5.2	

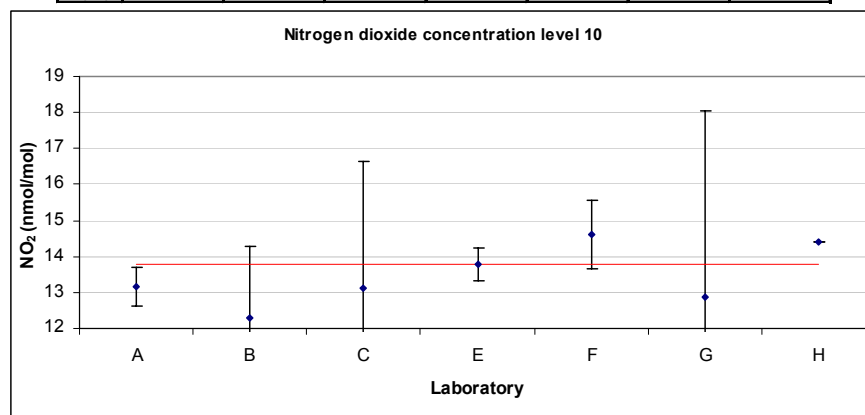


Figure 52: Reported values for NO₂ concentration level 10.

Annex C. The precision of standardized measurement methods

For the main purpose of monitoring trends between different IEs undertaken by ERLAP the precision of standardized SO₂, CO, O₃ and NO_x measurement methods [6], [8], [9] and [10] as implemented by NRLs was evaluated. Applied methodology is described in ISO 5725-1, -2 and -6 [19], [20] and [21]. The precision experiment has involved four laboratories, for NO_x, CO and SO₂ measurement methods, and five laboratories, for O₃ measurement method. Six concentration levels were tested, for O₃, CO, SO₂ and NO₂, and eleven for NO. The data consistency and outlier tests were uncertain due to the small number of participants, and no outliers were detected.

The repeatability standard deviation (s_r) was calculated in accordance with ISO 5725-2 as the square root of average within laboratory variance. The repeatability limit (r) is calculated using equation 8 [21]. It represents the biggest difference between two test results found on an identical test gas by one laboratory using the same apparatus within the shortest feasible time interval, that should not be exceeded on average more than once in 20 cases in the normal and correct operation of method.

$$r = t_{95\%,8} \cdot \sqrt{2} \cdot s_r \quad (8)$$

The reproducibility standard deviation (s_R) was calculated in accordance with ISO 5725-2 as the square root of sum of repeatability and between laboratory variance. The reproducibility limit (R) is calculated using equation 9 [21]. It represents the biggest difference between two measurements on an identical test gas reported by two laboratories, which should not occur on average more than once in 20 cases in the normal and correct operation of method.

$$R = t_{95\%,3} \cdot \sqrt{2} \cdot s_R \quad (9)$$

The repeatability standard deviation was evaluated with 8 (4·(3-1)) degrees of freedom (v) and reproducibility standard deviation with 3 (4-1) degrees of freedom. The critical range student factors ($t_{\alpha,v}$) are 2,31 and 3,18 respectively.

In

Table

47-

The reproducibility and repeatability of NO₂ measurements are dependant on both NO and NO₂ concentrations. In Table 51 both concentrations are given and in Figure 57, R and r are plotted as functions of NO₂ concentration.

Table 51 and Figure 53- Figure 57 the repeatability and reproducibility limits of measurement methods are presented (r, R). Also presented is ‘reproducibility from common criteria (R(from σ_p))’ calculated by substituting s_R in equation 8 with a ‘standard deviation for proficiency assessment’ (Table 3). Comparison between R and R(from σ_p) serves to indicate that σ_p is realistic ([18] 6.3.1) or from the other point of view, that the general methodology implemented by NRLs is fit for σ_p .

Table 47: The R and r of CO standard measurement method.

CO data ($\mu\text{mol/mol}$)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.002		0.05	
1.007	0.005	0.129	
1.979	0.013	0.364	
4.252	0.095	0.33	
5.881	0.082	0.412	
8.391	0.013	0.604	7.2%

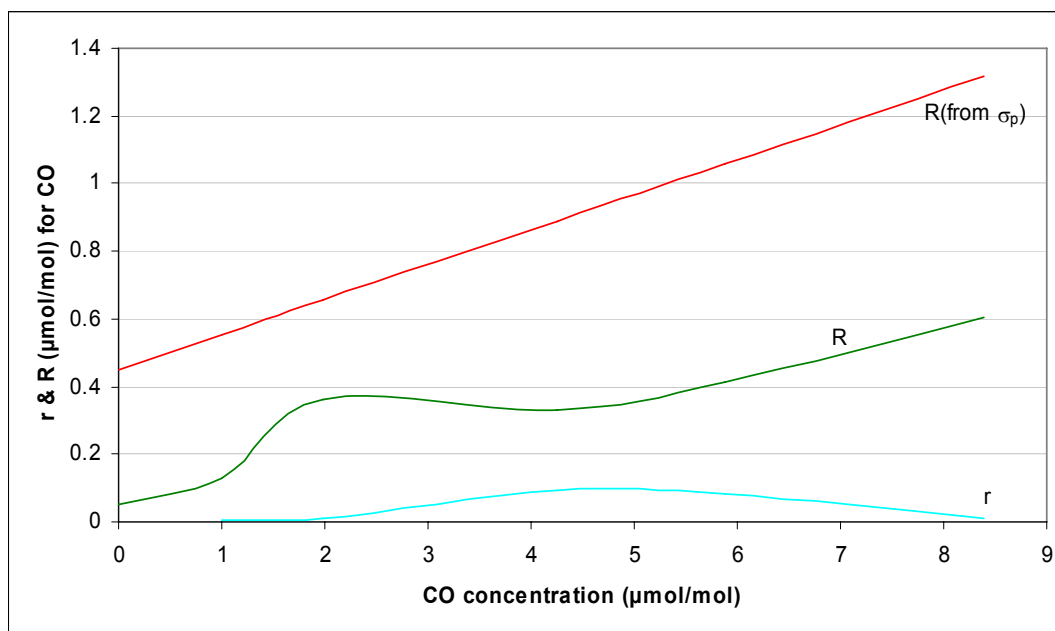


Figure 53: The R and r of CO standard measurement method as a function of concentration.

Table 48: The R and r of O₃ standard measurement method.

O ₃ data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2		1.2	
13.9	0.1	0.6	
21.3	0.1	1.1	
59.2	0.2	0.9	
99.8	1.4	1.8	
115.5	2.0	4.3	3.7%

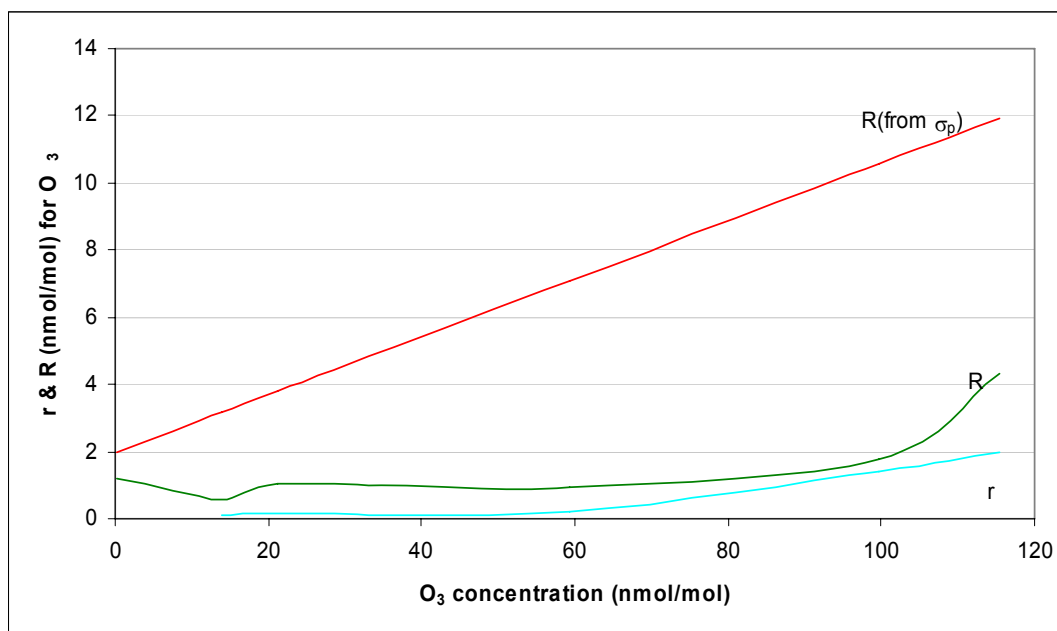


Figure 54: The R and r of O₃ standard measurement method as a function of concentration.

Table 49: The R and r of SO₂ standard measurement method.

SO ₂ data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.2		1.2	
3.2	0.3	0.8	
7.7	0.3	0.6	
18.2	0.3	1.5	
46.6	0.5	5.6	
131.3	0.5	17.3	13.2%

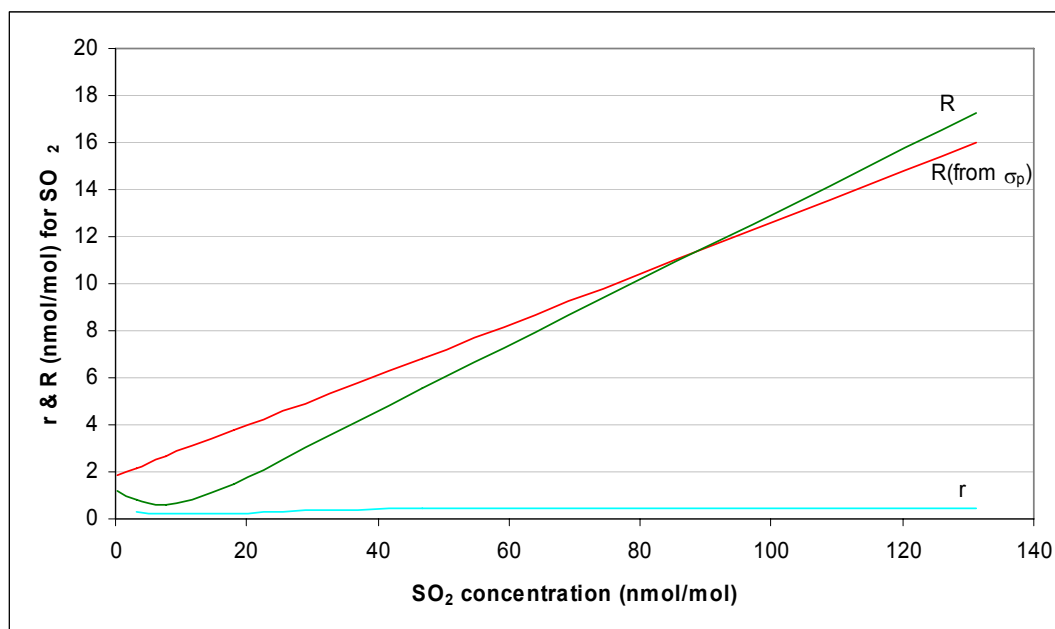


Figure 55: The R and r of SO₂ standard measurement method as a function of concentration.

Table 50: The R and r of NO standard measurement method.

NO data (nmol/mol)			
all data			
group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.3		0.7	
2.5	0.4	1.6	
15.6	0.6	2.9	
29.0	0.4	5.0	
49.6	0.3	6.6	
89.5	0.6	11.6	
148.1	0.8	14.4	
150.1	0.9	12.5	
248.4	1.3	21.5	
378.8	1.1	25.5	
494.6	2.2	44.3	
			9.0%

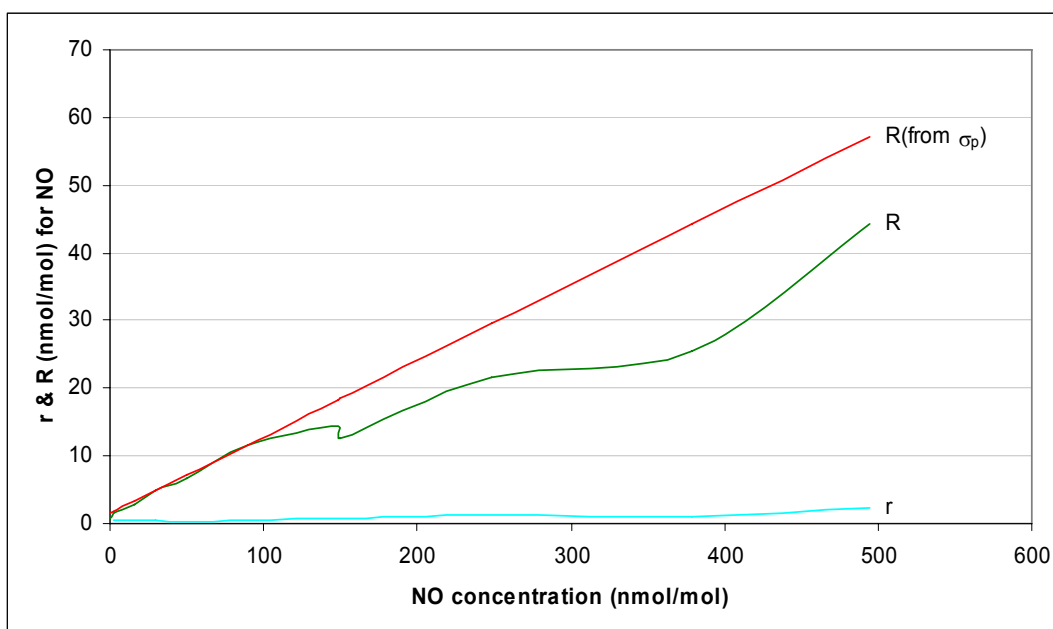


Figure 56: The R and r of NO standard measurement method as a function of concentration.

The reproducibility and repeatability of NO₂ measurements are dependant on both NO and NO₂ concentrations. In Table 51 both concentrations are given and in Figure 57, R and r are plotted as functions of NO₂ concentration.

Table 51: The R and r of NO₂ standard measurement method.

NO ₂ data (nmol/mol)				
all data				
NO	NO ₂	NO ₂		
group average	group average	repeatability limit : r	reproducibility limit : R	reproducibility limit (relative)
0.3	0.0		0.6	
2.5	13.1	0.7	2.9	
15.6	0.2	0.2	1.6	
29.0	21.0	0.5	2.2	
49.6	0.3	0.3	2.3	
89.5	59.5	0.8	3.3	
148.1	0.7	0.4	4.0	
150.1	101.3	0.5	4.3	
248.4	1.6	0.9	5.4	
378.8	119.8	1.2	5.7	4.8%
494.6	3.0	0.9	8.2	

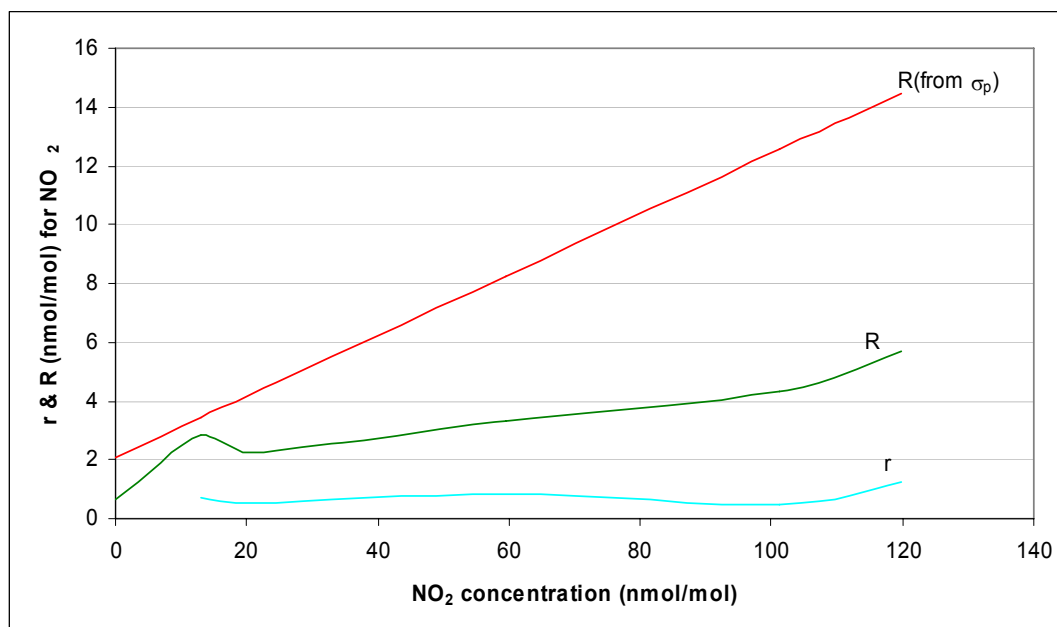


Figure 57: The R and r of NO₂ standard measurement method as a function of concentration.

European Commission

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Abstract

From the 13th to the 16th of October 2008 in Ispra (IT), 5 AQUILA (Network of European Air Quality Reference Laboratories) and 2 laboratories of the World Health Organisations (WHO) Euro-Region met at an intercomparison exercise to evaluate their proficiency in the analysis of inorganic gaseous pollutants covered by European Air Quality Directives (SO₂, CO, NO, NO₂ and O₃).

The proficiency evaluation, where each participant's bias was compared to two criteria, provides information on the current situation and capabilities to the European Commission and can be used by participants in their quality control system.

In terms of criteria imposed by the European Commission, 44% of the results reported by AQUILA laboratories were good both in terms of measured values and reported uncertainties. Another 56% of the results had good measured values, but the reported uncertainties were either too small (54%) or too high (2%).

The comparability of results among AQUILA participants is satisfactory for O₃, CO, NO₂ and NO measurement method, but the pollutant SO₂ needs further improvements and harmonization programmes.

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